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HAZE FORMATION -- ITS NATURE AND ORIGIN

William E. Wilson, Jr., et al

Battelle Columbus Laboratories
Columbus, Ohio

28 January 1972

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Battelle analyzed aerosols obtained in New York City, Great Smoky Mountains, in laboratory smog chamber facilities, and from primary automobile exhaust. The results indicated that certain organic chemicals were present in aerosols associated with auto exhaust which were not present in aerosols from rural atmospheres. On the other hand, at least one organic compound was present in aerosols from rural atmospheres which was not present in urban air aerosol samples. These results indicate that the presence of certain organic compounds in aerosol samples may indicate the origin of haze.

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Haze
Toluene
Aerosol
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Ozone

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New York City
Smoky Mountains
α-Pinene

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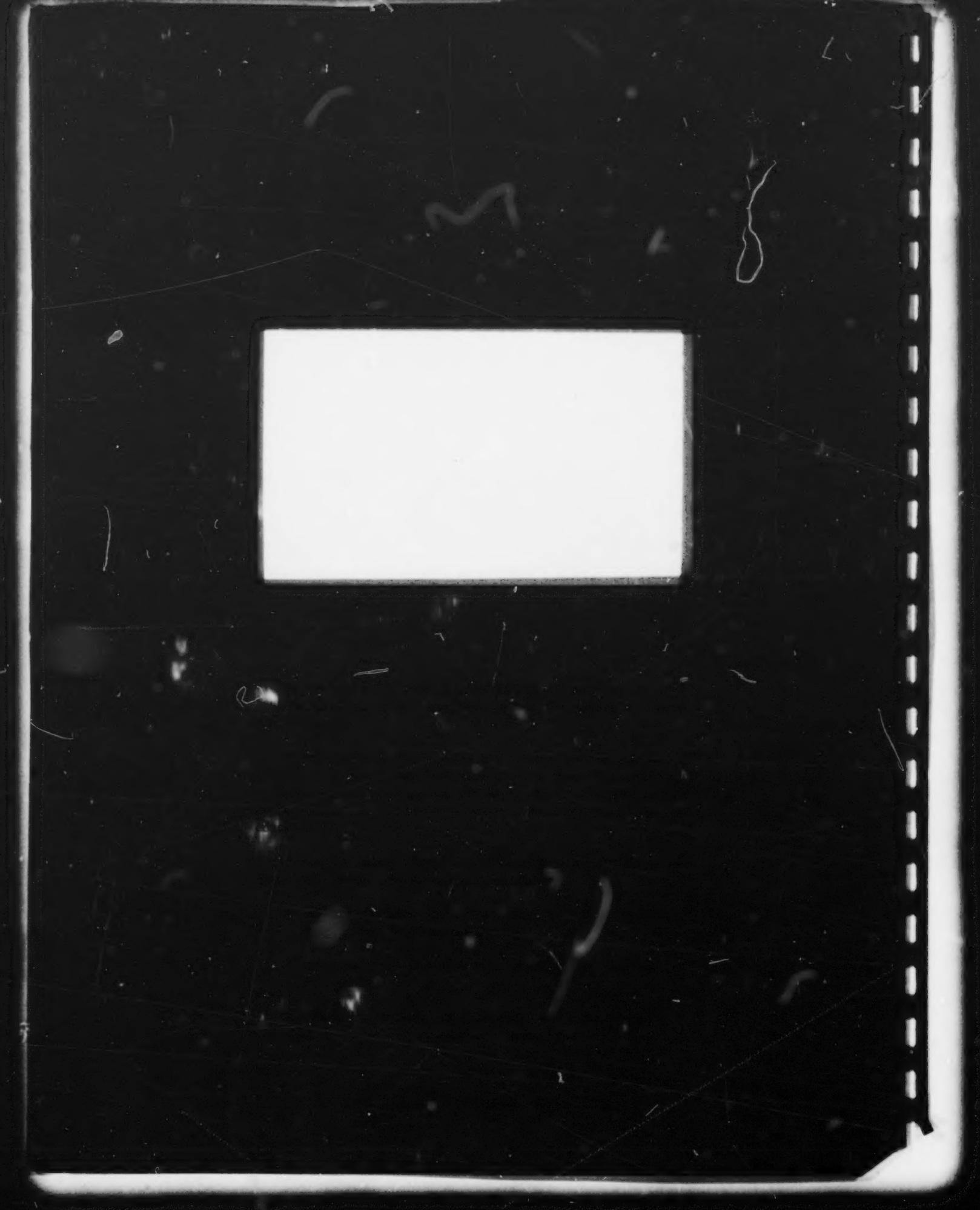

HAZE FORMATION -- ITS NATURE AND ORIGIN

to

ENVIRONMENTAL PROTECTION AGENCY
CPA 70-Neg. 172

and

COORDINATING RESEARCH COUNCIL
CAPA 6-68

by

Wm. E. Wilson, Jr., Warren E. Schwartz,
and G. W. Kinzer

January 28, 1972

II

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FINAL REPORT

on

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INTRODUCTION

The ultimate goal of this program is the development of a field technique capable of elucidating the contribution of automobile exhaust to atmospheric haze. To attain this goal, it is necessary to establish the relationship between atmospheric haze and automotive emissions and to discover methods for distinguishing between the man-made and natural hazes. Experimental studies involve measurements of the optical and chemical properties of the atmospheric aerosol and determination of the gaseous pollutants in the atmosphere in which the aerosol is found. As a result of the first year's study, significant insight has been gained in understanding the nature and magnitude of the problems inherent in specifying the contributing sources for haze.

SUMMARY AND CONCLUSIONS

The objective of the first year's program was to determine if the organic composition of atmospheric aerosols could be used to identify

their sources. Particulate associated with the following sources was collected for analysis:

(1) urban and rural atmospheric haze

(2) primary auto exhaust

(3) aerosol generated from known precursers in the Battelle-Columbus smog chamber.

Field sampling of haze particles was performed at two locations in New York City and in the Blue Ridge Mountains. Samples were collected at the Bronx State Hospital grounds during the full month of September, 1970. From September 21, through October 2, 1971, samples were also collected in mid-Manhattan on the rooftop (fifth floor) of the Cooper Union Building. Battelle's mobile laboratory was then moved to the Blue Ridge Mountains, where continuous sampling was conducted from October 12 to October 23, 1970.

The collections of air-borne particles were made with two hi-vol samplers, one conventionally designed and one equipped with a cyclone, (see Cyclone Design and Performance Evaluation) which "cut out" nonrespirable and nonlight-scattering particles (> 2 microns). Samples were obtained on both glass and nylon fiber filters.

At all three sites, simultaneous measurement of visibility reduction was made with an integrating nephelometer. Concurrent measurements of the gas phase components were expected to have been made at the Bronx site by Scott Laboratories, but scheduling precluded the collection of most of those data. Monitoring in the Blue Ridge Mountains included sunlight intensity, relative humidity, ozone concentration, condensation nuclei count, and light scattering with a multiwavelength integrating nephelometer.

Histographs made of the light scattering data from the sampling sites showed that the average visibility during the sampling periods was 40 miles for the Blue Ridge Mountain site, 12 miles for the Bronx site, and 9 miles for the Manhattan site. The most severe visibility conditions recorded at the respective sites were 14, 5, and 3 miles.

The detection of a terpene oxidation product in the Blue Ridge Mountain aerosol and the relationships observed between light scattering, sunlight, and ozone formation confirmed the notion that the blue haze is a photochemical aerosol fueled in part by the terpene emissions from trees.

The engine-exhaust aerosol was generated from a 1967 Chevrolet operated on a chassis dynamometer. The exhaust from one 7-mode Federal driving cycle was vented into a large (300 cu ft) Mylar bag containing sufficient dry nitrogen to prevent condensation of water vapor. The engine aerosol (primary) was collected by evacuating the bag through a glass-fiber filter.

The aerosols generated from individual hydrocarbons were prepared in a 610-cu-ft environmental chamber by irradiating 10 ppm of selected hydrocarbon and 1 ppm of NO_2 in clean, humidified (50 percent RH) air. Measurements of visibility reduction and oxidant concentration were used to indicate the progress and extent of the smog formation. After the maximum ozone concentration had been reached, the chamber contents were evacuated through glass fiber filters. Several such runs were made with each of the following hydrocarbons: α-pinene, cyclohexene, 1-heptene, and toluene.

Preliminary analysis involved infrared spectroscopic examination of particulate samples on millipore paper for use with a dual beam spectrophotometer. Infrared spectroscopic analysis was also carried out on organic extracts of particulate. Analysis revealed the presence of various chemical classes and provided general information on similarities and differences in particulate matter from various sources. Subsequent analyses were of a more detailed nature and involved chemical fractionation of particulate extracts and identification of specific components by gas chromatography (GC) and gas chromatography combined with mass spectroscopy (GC-MS).

Analyses of urban aerosol and primary auto exhaust particulate were directed toward the elucidation of <u>differences</u> between the organic fractions of aerosol from the two sources. Specifically compounds were sought which might be utilized as "fingerprints" of primary auto exhaust to aid in establishing the automotive contribution to urban haze. Analyses of the organic fraction of auto exhaust particulate by GC-MS revealed the presence of benzoic acid and phenylacetic acid. These aromatic acids were not detected in urban air particulate carried through the same analytical procedure. The observations may be explained in terms of dilution of auto exhaust in the atmosphere, or on the basis of removal of these acids from the atmosphere by (secondary) photochemical reactions.

A variety of other important differences between auto exhaust and urban aerosol were determined. The concentration of aldehydes, ketones, esters, and organic acids in urban aerosol is an order of magnitude greater than that found in auto exhaust particulate. Presumably, the higher concentration of oxygenates in urban aerosol results, at least in part, from atmospheric reactions of hydrocarbons. Such a finding is consistent with our studies of hydrocarbons reacted under simulated atmospheric conditions. Two general types of reactions were observed, oxidative cleavage of a carbon-carbon multiple bond, and oxidative decarboxylation.

Analyses of natural haze aerosol (Blue-Ridge Mountains site) revealed a far lower concentration (~ 10 percent) of long chain carboxylic acid than found in urban aerosol. This most likely reflects the presence of urban sources contributing such organic acid pollulants or their (reduced) precursors to the atmosphere.

The smog chamber reactions of α-pinene typify the types of reactions observed under simulated atmospheric conditions. This natural terpene is produced in large quantities by plants and trees, and is found in the forest atmosphere. Under conditions of the smog chamber it undergoes oxidative cleavage to pinonic acid. Further reaction yields "nor-pinonic" acid by oxidative decarboxylation. It is most significant that analyses of natural haze aerosol revealed the presence of pinonic acid. Pinonic acid was not found in urban aerosol carried through the same analytical procedure. Ultra-low levels of this acid in urban aerosol might be determined by ion-specific spectrometry. The level of pinonic acid in urban atmosphere might be used as a measure of the contribution of natural haze to urban smog where a forested region is contiguous to an urban center. Finally, it should be noted, that the finding of pinonic acid in both natural haze and smog chamber reaction products tends to indicate that the smog chamber operating parameters used in this study generate oxidizing conditions.

Details concerning the elucidation of reactions observed under simulated atmospheric conditions are presented in the report section on

Analysis of Smog Chamber Aerosol. An especially noteworthy result of this phase of the research, however, was the finding of an organic nitrate reaction product of cyclohexene. This finding reveals another sink for nitrogen oxides and should help in establishing a better nitrogen balance.

EXPERIMENTAL

SAMPLING SITES

Field sampling of haze particles was performed at two locations in New York City and in the Blue Ridge Mountains. Samples were collected at the Bronx State Hospital grounds during the full month of September, 1970. From September 21, through October 2, 1971, samples were also collected in mid-Manhattan on the rooftop (fifth floor) of the Cooper-Union Building. Battelle's mobile laboratory was then moved to the Blue Ridge Mountains where continuous sampling was conducted from October 12, to October 23, 1970.

Bronx Site

The originally scheduled sampling site was in the Bronx, New York City, on the grounds of the Bronx State Hospital. This location was chosen because Scott Research Labs were conducting a gas phase monitoring program at the same location for the Coordinating Research Council. The site selection was based on the fact that the Bureau of Abatement, Environmental Protection Agency, had previously monitored at that site.

This site proved to be less than adequate for aerosol studies. The site was near the eastern edge of the Bronx, close to Pelham Bay. As a result, in the morning the air was generally clear due to a shore breeze from the Bay. In the afternoon the wind would change and aged pollutants from other areas of New York City would be convected to the site. The trailer was located adjacent to a sewage pumping and chlorination station

on the hospital grounds. There were apparently occasional leaks which contributed to nighttime and unexpectedly high oxidant readings. The site was located across the street from an area used for storage and repair of trains used in the New York subway system. Within a three block radius there was an elevated line, an expressway, two power plants for the State Hospital, a bakery, and a bulk oil and coal depot.

Due to instrument difficulties and scheduling problems the Scott Research Lab monitoring effort was unable to obtain good measurements of CO until well into the month of September. Since this was a critical parameter for relating aerosol concentrations to auto exhaust emissions, it does not seem useful to list in detail other measurements since they are valueless without the CO data.

Due to inadequacies of the site both in terms of continuous aerosol monitoring and in the unrepresentative nature of the collected aerosol, it was decided to move the monitoring instruments to a site in downtown Manhatten. However, hi-vol samples were collected continuously at the Bronx site during the month of September.

Cooper Union Site

Arrangements were made through the New York City Air Pollution Agency, in cooperation with Cooper Union, to set up a monitoring station on the fifth floor roof of the Engineering Building of Cooper Union at 51 Astor Place. This station was adjacent to the New York City Air Pollution Agency's offices and laboratory. Integrating nephelometer measurements and total particulate collections were made at this site during the last two weeks of September. The building was located at the intersection of three major traffic arteries. However, due to the height there should have been good mixing of auto exhaust. Two power plants were visible from the roof but they were not close enough to make a predominant contribution to the particulate matter collection. There did not appear to be any other strong sources in the immediate neighborhood.

Blue Ridge Mountain Site

At the end of September the sampling instruments were put back into the trailer and the trailer was moved to a site in the Blue Ridge Mountains in North Carolina. The site was located in the Pisgah National Forest about 30 miles northeast of Ashville, North Carolina. It was located between the two ranges of the Appalachian Mountains approximately 5 miles east of Mount Mitchell and 2 miles northwest of the Blue Ridge Parkway at an altitude of 3600 ft. There was extensive evergreen and hardwood forest cover. The trailer was located 50 feet from a gravel road. Traffic consisted of only a few cars a day. The site was one mile from the Black Mountain Campground but except on weekends there were only 1 or 2 campers. (The site originally planned for was 5 miles from the campground but this turned out to be on a hill below the gravel road situated so that the dust cloud from the road was at the same height and less than 25 feet from the intake ducts. It was therefore necessary to relocate after observing the original site.) There were only a few houses within a 5-mile radius of the site. The nearest community was Micaville which was 15 miles away. Mount Mitchell and the mountain ranges protected the site from pollution from any of the urban centers which would have caused difficulties had the site been located outside the two ranges.

COLLECTION AND GENERATION OF AEROSOL

The collections of air-borne particles were made with two hi-vol samplers, one conventionally designed and one equipped with a cyclone which "cut out" nonrespirable and nonlight-scattering particles (> 2 microns). The performance characteristics of the cyclone are presented under Cyclone Design and Performance Evaluation, pages 9 - 14. Samples were obtained on both glass and nylon fiber filters.

At all three sites, simultaneous measurement of visibility reduction was made with an integrating nephelometer. Concurrent measurements of the gas phase components were expected to have been made at the

the Bronx site by Scott Laboratories, but scheduling precluded the collection of most of that data. Monitoring in the Blue Ridge Mountains included sunlight intensity, relative humidity, ozone concentration, condensation nuclei count, and light scattering with an integrating nephelometer.

Samples of light-scattering particles produced under controlled conditions in the laboratory were collected with similar facilities (hi-vol samplers). The laboratory aerosols were generated from two unambiguous sources, primary automobile exhaust and irradiated NO_2-hydrocarbon mixtures.

The engine-exhaust aerosol was generated from a 1967 Chevrolet automobile operated on a chassis dynamometer. The exhaust from one 7-mode Federal driving cycle was vented into a large (300-cu-ft) Mylar bag containing sufficient dry nitrogen to prevent condensation of water vapor. The engine aerosol (primary) was collected by evacuating the bag through a glass-fiber filter.

The aerosols generated from individual hydrocarbons were prepared in a 610-cu-ft environmental chamber by irradiating 10 ppm (v/v) selected hydrocarbon and 2 ppm of NO_x in clean, humidified air. Measurements of visibility reduction and oxidant concentration were used to indicate the progress and extent of the smog formation. After the maximum aerosol concentration had been reached, the chamber contents were evacuated through glass fiber filters. Several such runs were made with each of the following hydrocarbons: α-pinene, cyclohexene, 1-heptene, and toluene.

ORGANIC ANALYTICAL PROCEDURES

The organic fraction of the particulate was obtained by Soxhlet extraction with "distilled-in-glass" methylene chloride[1] for 6 hours. Approximately 20 ml of solvent was used for each 4-inch filter disc. Typically, the methylene chloride was distilled off and the residue weighed. The "organic soluble residue" thus obtained was used for subsequent fractionation and analysis.

Gas chromatography interfaced with mass spectrometry (GC-MS) was frequently employed in the analysis of materials isolated from particulate matter or smog chamber aerosol. The instrument employed was a Finnigan 1015 Quadrupole Mass Spectrometer. The ion source of this instrument has been modified to permit the generation of either electron impact or chemical ionization mass spectra. Instrument control and data acquisition are accomplished using an interfaced digital computer. The reconstructed gas chromatograms shown in this report are computer generated. The detector response in such chromatograms is derived from integrated total ion-current obtained during successive scans on the mass spectrometer. The complete mass spectrum obtained during any given scan can be recalled from memory (tape) by reference to a Spectrum Number along the x-axis of the reconstructed gas chromatogram.

RESULTS AND DISCUSSION

CYCLONE DESIGN AND PERFORMANCE EVALUATION

A simple cyclone having a tangential air-flow inlet was designed and evaluated for use as a precollector for large particles and for use upstream of the filter. The intent of the cyclone was to remove atmospheric particles that, because of their large size, were not effective in

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(1) Obtained from Burdic and Jackson, Muskegon, Michigan.

contributing to visibility reduction or the optical properties of haze. This upper limit for haze particles was arbitrarily chosen to be about 2 μm. Hence, the cyclone was intended to remove particles larger than 2 μm at the flow rate of the sampling system.

Because the particle-collecting ability of a cyclone is dependent on volumetric gas flow rate, the cyclone design was checked analytically to be sure that the total system pressure loss (pressure loss in the cyclone plus loss in the filter) was not so large that the capabilities of the blower were exceeded.

The design procedure for a simple cyclone having a tangential air inlet was taken from the standard design equations as given in the Chemical Engineers Handbook.[2] A sketch of the general design of the cyclone and the relationships between the dimensions are given in Figure 1. Because the dimensions are all specifically related, the design is based on only one dimension from which the others are then scaled. The characteristic cut-off size, D_{pc}, for the cyclone is given by:[2]

$$D_{pc} = \sqrt{\frac{9\mu B_c}{2\pi N_e V_c (\rho_p - \rho)}} \qquad (1)$$

where:

B_c = width of inlet duct, cm

N_e = factor depending on inlet geometry and flow rate, approximately equal to 5

V_c = inlet gas velocity, cm/sec

ρ_p = density of particle material, gm/cm^3

ρ = density of gas, gm/cm^3

D_{pc} = diameter of particle defined as characteristic cut-off size, cm

μ = viscosity of gas, poise.

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(2) Perry, J. H., Editor, Chemical Engineers Handbook, 3rd Edition, McGraw-Hill Book Company, Inc., New York (1950), pp 1024-1026.

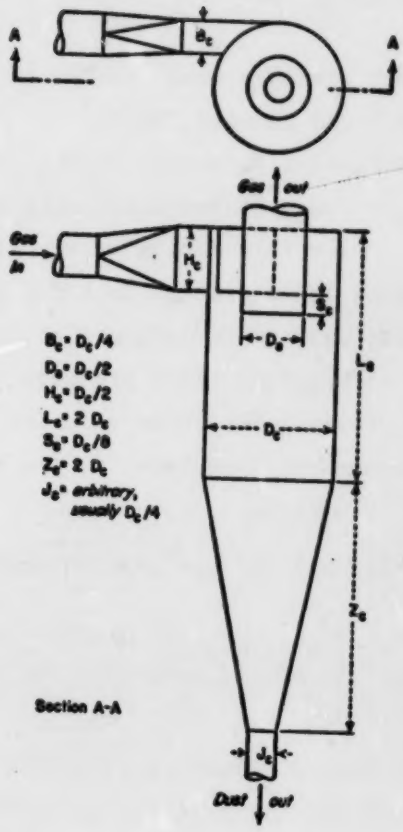

FIGURE 1. CYCLONE SEPARATOR PROPORTIONS

The characteristic cut-off size is defined as the diameter of those particles collected by the cyclone with an efficiency of 50 percent.

The pressure loss in a cyclone of this design is given as:(1)

$$\Delta P = F_{cv} \left[0.0030\ \rho^* \ (V_c^*)^2\right] \qquad (2)$$

where:

ΔP = pressure loss, inches of water

ρ^* = gas density, lb/ft^3

V^* = inlet velocity, ft/sec

F_{cv} = constant characteristic of cyclone geometry which for this design is reported to have a value of 8.

An additional consideration is the volumetric flow rate desired for sampling. In this case 20 ft^3/min was chosen as being reasonable from considerations of sampling time, pressure loss, and capacity of the high-volume sampler blower. The inlet velocity to the cyclone, V_c, is given in terms of volumetric flow rate, Q, and cyclone dimensions as:

$$V_c = Q/2B_c^2. \qquad (3)$$

Equations (1) and (3) can then be combined to give

$$B_c = \left[\frac{\pi Q N_e (\rho_p - \rho) D_{pc}^2}{9\mu}\right]^{1/3}. \qquad (4)$$

If a cut-off size of 2μm, a volumetric sampling rate of 20 ft^3/min, and the appropriate values for the physical properties of air are assumed, the dimension B_c can be found to be 1.54 cm or 0.6 inch. The pressure loss in the cyclone for these conditions is predicted with Equation (2) to be 14.4 mm Hg. The dimensions for the cyclone are:

B_c = 0.60 inch	L_c = 4.80 inches
D_c = 2.40 inches	S_c = 0.30 inch
D_e = 1.2 inches	Z_c = 4.80 inches
H = 1.20 inches	J_c = 0.60 inch.

The cyclone was constructed to these specifications from stainless steel.

Because the cyclone design procedure may not be accurate for small particles, it was felt that the design should be evaluated after the cyclone was constructed. Calibrations were performed with two test aerosols, dyed water droplets and a selected portion of small, dry dust particles separated from A.C. Test Dust, Fine.

The water aerosol with uranine dye tracer added was produced with a DeVilbiss D-40 nebulizer operating with the side port closed and at an air pressure of 5 psig. The size distribution of the resulting aerosol was measured using fluorometric techniques and a Battelle cascade impactor. Three determinations of the size distribution were made and are in excellent agreement as shown in Figure 2.

A.C. Test Dust, Fine was separated in a BAHCO particle classifier and those particles separated as being smaller than 10.4 μm were used to form the dust aerosol. This fraction of small particles was then aspirated into an airstream for use as a test aerosol. The size distribution of dry dust particles used in this case was determined with a Coulter Counter and this distribution is shown in Figure 2.

The efficiency of the cyclone was determined for each test aerosol by analyzing, either fluorometrically or by weight, for the amount collected on a glass fiber filter downstream of the cyclone. The glass fiber filter was MSA 1106B and should have an efficiency of essentially 100 percent for the particle sizes of interest in this study.

Three determinations with the water plus dye aerosol gave cyclone efficiencies of 82, 89, and 85 percent. Two determinations with the dry dust gave efficiencies of 89 and 84 percent. The mass mean size for the water plus dye aerosol was 2.4 μm and for the dust was about 5 μm. Although an exact determination of cut-off size was not made, it is estimated from comparisons between the size distributions and cyclone efficiencies that for the water aerosol the cut-off size, D_{pc}, is about 1 μm or slightly less. For the dry dust the cut-off size is about 2.5 μm. The lower efficiency for the dry dust as compared with the water plus dye aerosol is undoubtedly the result of reentrainment from the walls of the

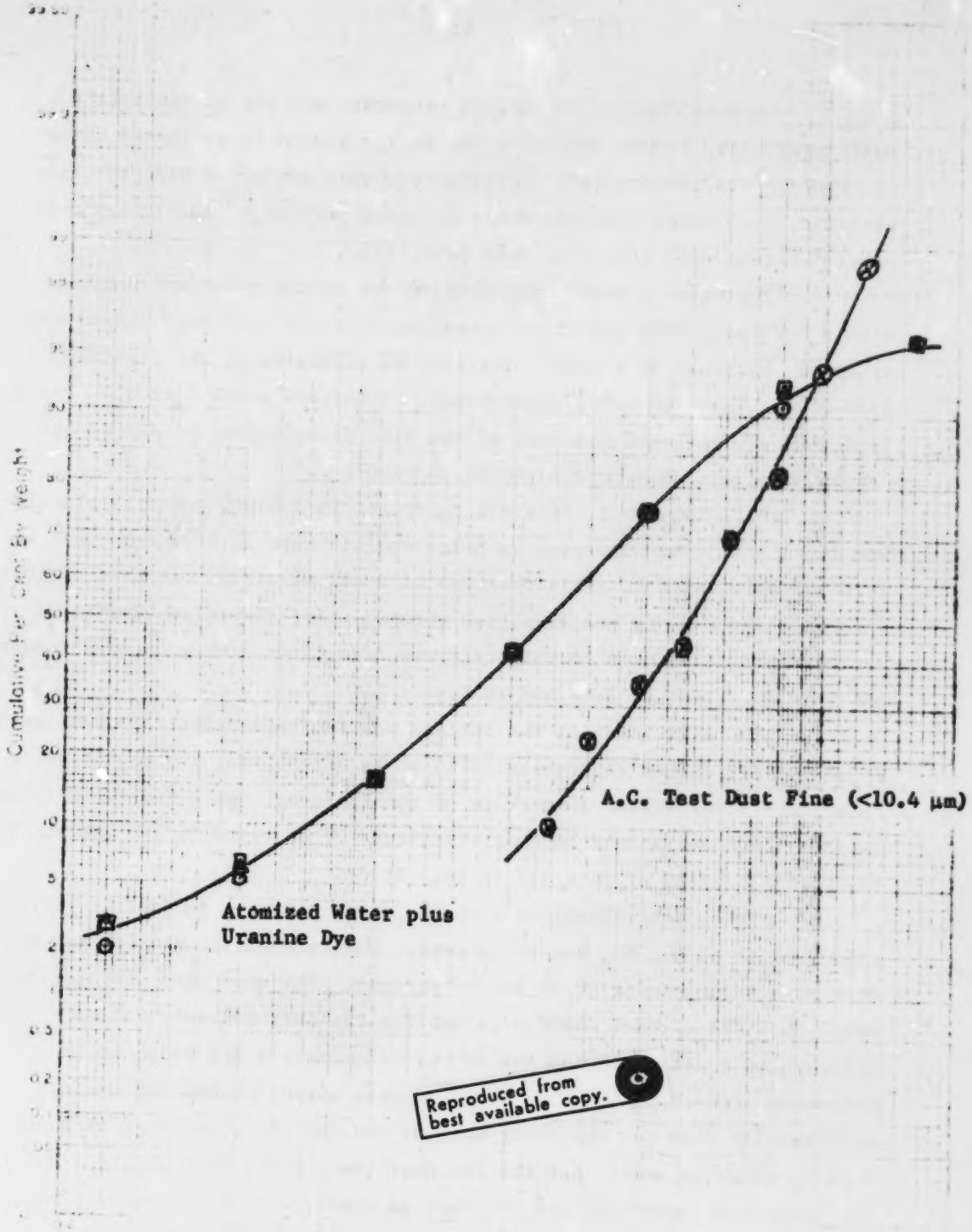

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FIGURE 2. SIZE DISTRIBUTIONS OF TEST AEROSOLS

cyclone for the dry dust. Reentrainment is known to become significant for small diameter cyclones and apparently is significant enough to overcome the effects of material density. In either case it appears that the cyclone operated in approximately the predicted manner and gave cut-off sizes near the design value of 2 μm.

LIGHT SCATTERING STUDIES

Light scattering studies were made at the three sampling sites with an integrating nephelometer. Histographs are shown in Figure 3. Average visibility during the periods studied was 40 miles for the Blue Ridge Mountains site, 12 miles for the Bronx site, and 9 miles for the Manhattan site. As shown on the histograph, visibility in the Blue Ridge Mountains was never less than 14 miles. The blue haze is noticeable because there are many vistas where mountain ranges can be seen 50 to 60 miles in the distance. The lowest visibility recorded at the Bronx site was 5 miles and at Cooper-Union, 3 miles.

Observations of terpenes by gas chromatography and of ozone by Regner and Mast instruments tend to indicate that the blue haze is a photochemical aerosol generated from terprene emissions from trees. Several profiles showing the relationships of light scattering, sunlight, and ozone observed in the Blue Ridge Mountains are shown in Figure 4. Two light scattering profiles from the Cooper-Union site are shown in Figure 5. These illustrate the effect of different meteorological conditions.

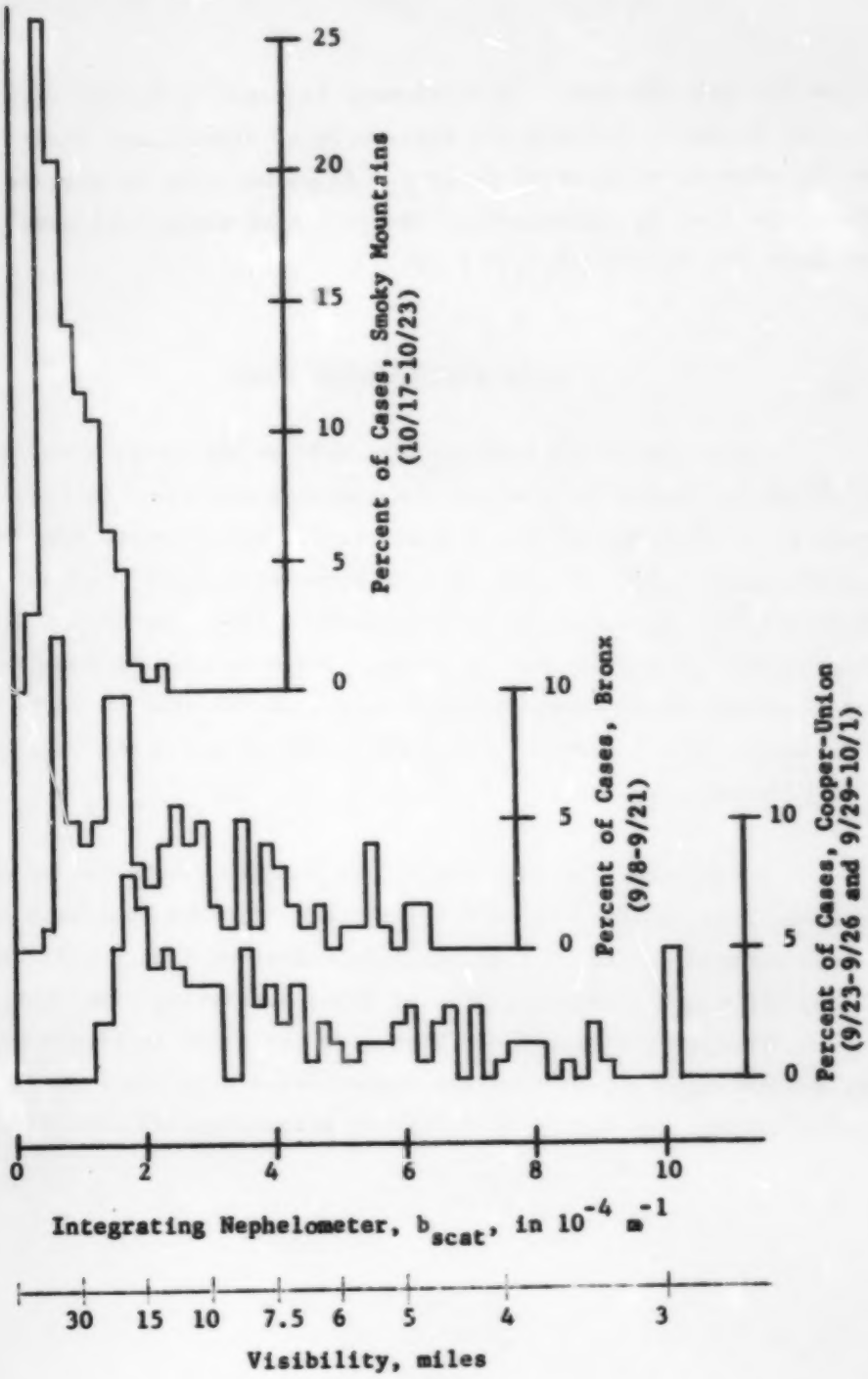


FIGURE 3. FREQUENCY DISTRIBUTION OF VALUES OF VISUAL RANGE MEASURED BY AN INTEGRATING NEPHELOMETER AT THREE SAMPLING SITES: BRONX, N.Y., MID-MANHATTAN, N.Y. (COOPER-UNION BLDG), AND BLUE RIDGE MOUNTAINS

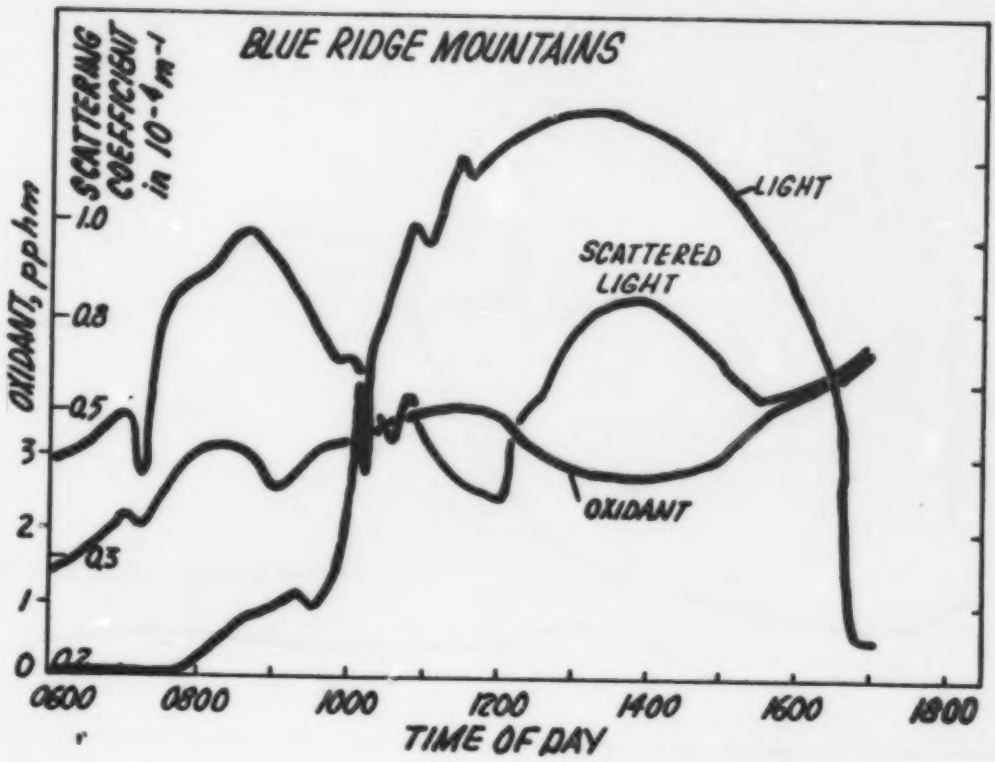


FIGURE 4. DAYTIME-CONCENTRATION PROFILE OF THE SUNLIGHT INTENSITY, OZONE, AND LIGHT-SCATTERING RELATIONSHIPS OBSERVED IN THE BLUE RIDGE MOUNTAINS.

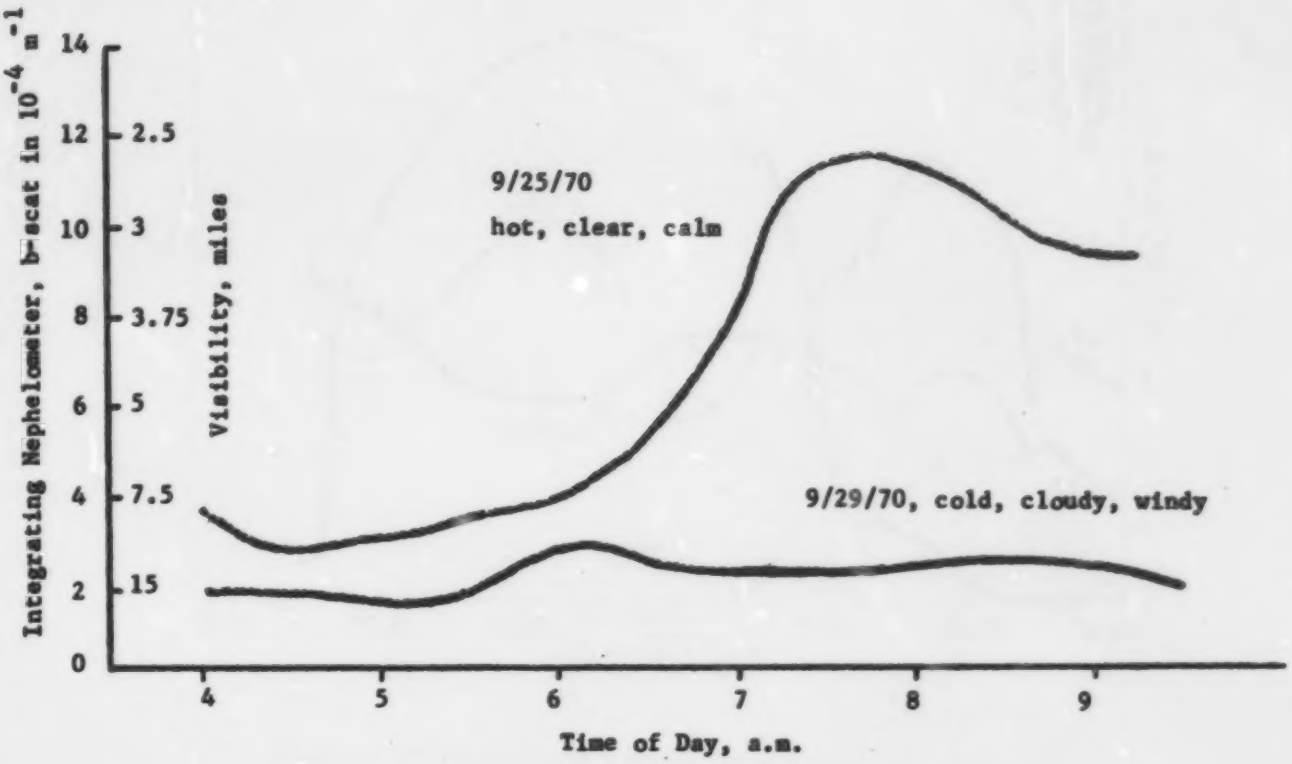


FIGURE 5. EFFECT OF METEOROLOGICAL CONDITIONS ON VISIBILITY IN MANHATTAN (COOPER-UNION SITE)

ORGANIC ANALYTICAL STUDIES

Infrared Spectroscopic Analysis of Total Particulate

The use of infrared spectra to give information about the organic content of aerosols was investigated. Particulate samples associated with urban and rural atmospheric aerosol and auto exhaust were examined. Aerosols generated in the smog chamber from straight chain and monocyclic olefins and aromatics were also examined. (Earlier studies[3,4] describe the formation of aerosol from cyclic and bicyclic olefins.) Infrared spectra obtained from aerosol particles collected directly on Millipore filter paper (ultrathin type TH, 0.45 μm) are shown in Figures 6 through 10.

Spectra of aerosols generated from cyclohexene/NO_x and m-xylene/NO_x are shown in Figure 6. Absorption bands due to the OH stretch in organic acids, the CH stretch, and the carbonyl C=O stretch can be identified. The low frequency part of the doublet at about 6 microns is due either to C=C or organic nitrates. The similarity between the cyclohexene and the m-xylene spectra is evident. In addition to the organic absorption bands, other features may be attributed to NH_4^+ and possibly $SO_4^=$ and NO_3^-.

In Figure 7 spectra are compared from 1-heptene/NO_x and from 1-heptene/NO_x/SO_2. Several new peaks can be seen in the spectrum of the aerosol from the SO_2 containing system. The infrared spectra of the methylene chloride extracts however are identical, indicating that the additional material in the SO_2-containing aerosol is possibly inorganic.

A comparison of the spectra of primary and secondary aerosols from auto exhaust is shown in Figure 8. The relative reduction of CH

(3) Groblicki, P. J., and Nebel, G. J., "The Photochemical Formation of Aerosols in Urban Atmospheres", General Motors Corporation Research Publication GMR-957, October 6-7, 1969.

(4) Endow, H., Doyle, G. J., and Jones, J. L., "The Nature of Some Model Photochemical Aerosols, JAPCA, 13, 141 (1963).

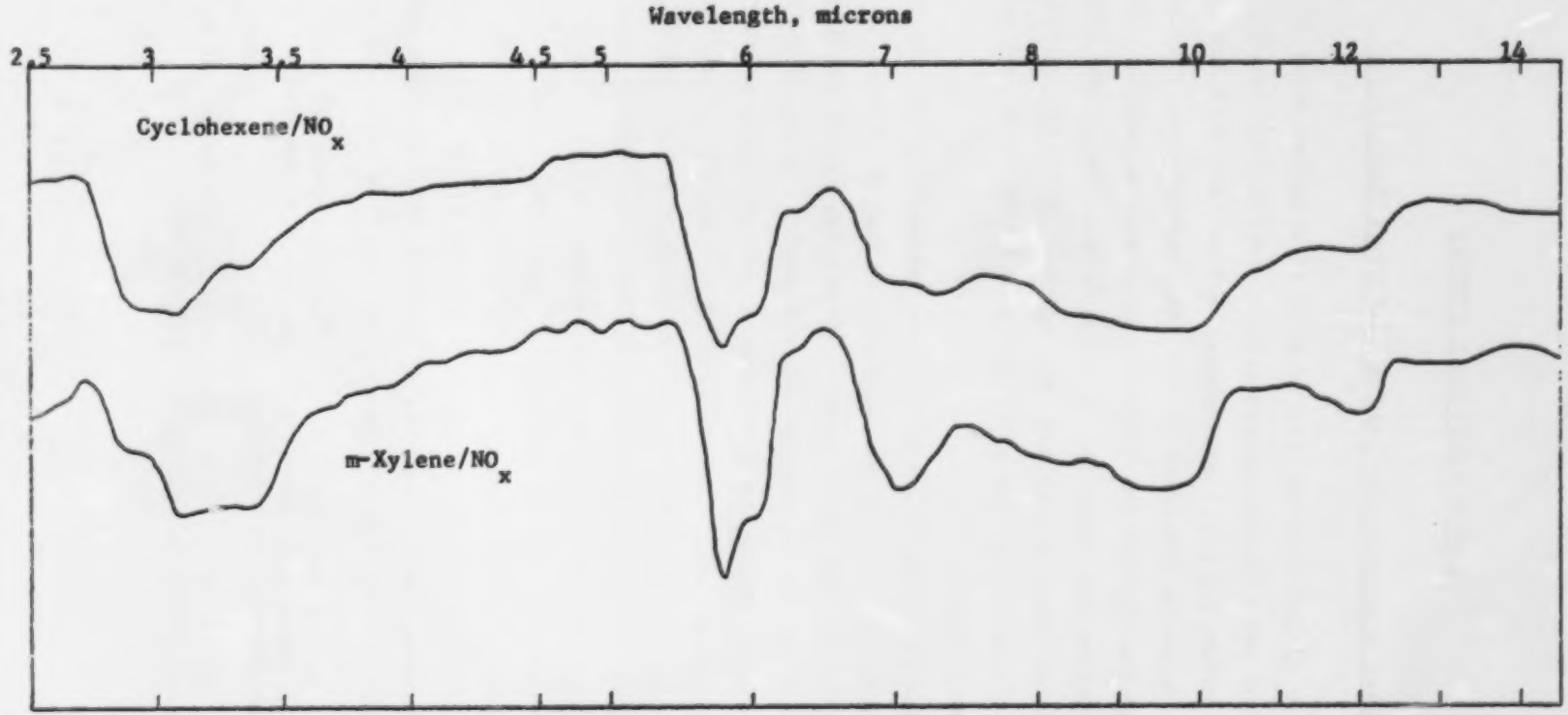


FIGURE 6. INFRARED SPECTRA OF AEROSOLS GENERATED FROM CYCLOHEXENE/NO$_x$ AND M-XYLENE/NO$_x$

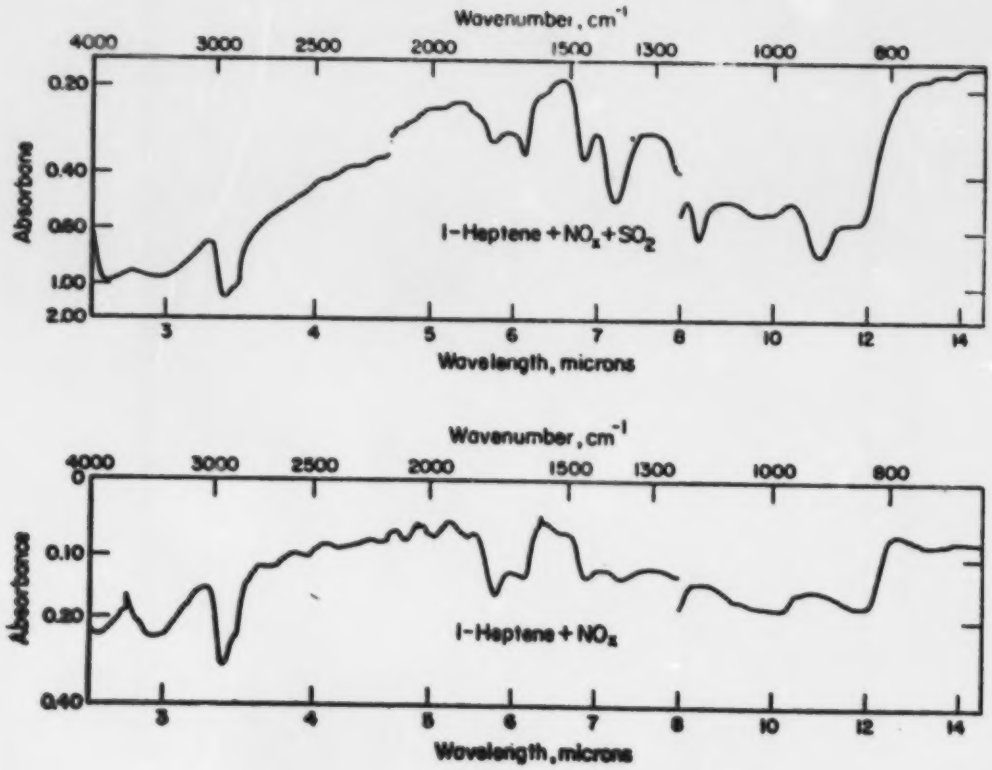


FIGURE 7. DETERMINATION BY INFRARED ANALYSIS OF THE EFFECT OF ADDED SO_2 ON THE CHEMICAL COMPOSITION OF AEROSOL GENERATED FROM AN IRRADIATED MIXTURE OF 1-HEPTENE-NO_x.

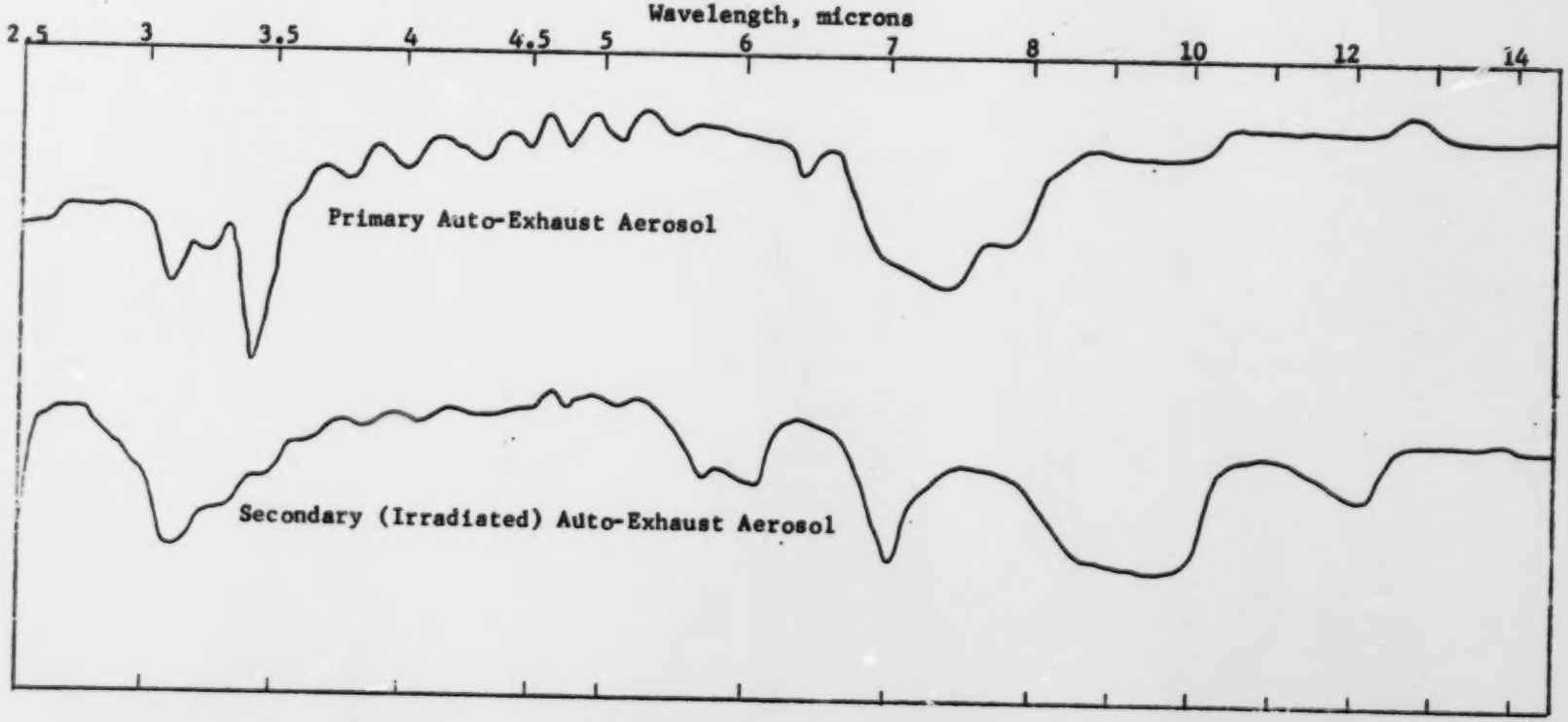


FIGURE 8. INFRARED SPECTRA OF PRIMARY AND SECONDARY AUTO-EXHAUST AEROSOL

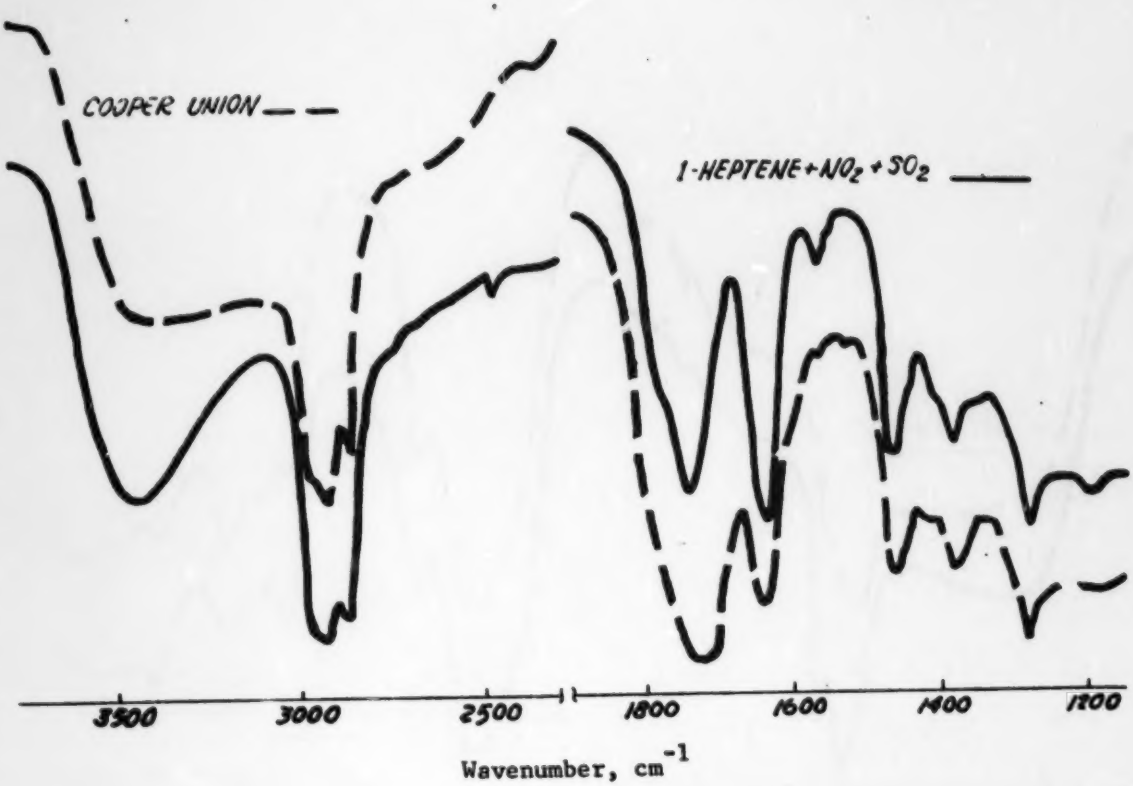


FIGURE 9. COMPARATIVE INFRARED ABSORPTION BANDS OF AEROSOL GENERATED FROM KNOWN PRECURSORS (1-HEPTENE-NO_x) AND FROM COMPLEX MIXTURES OF URBAN SOURCES

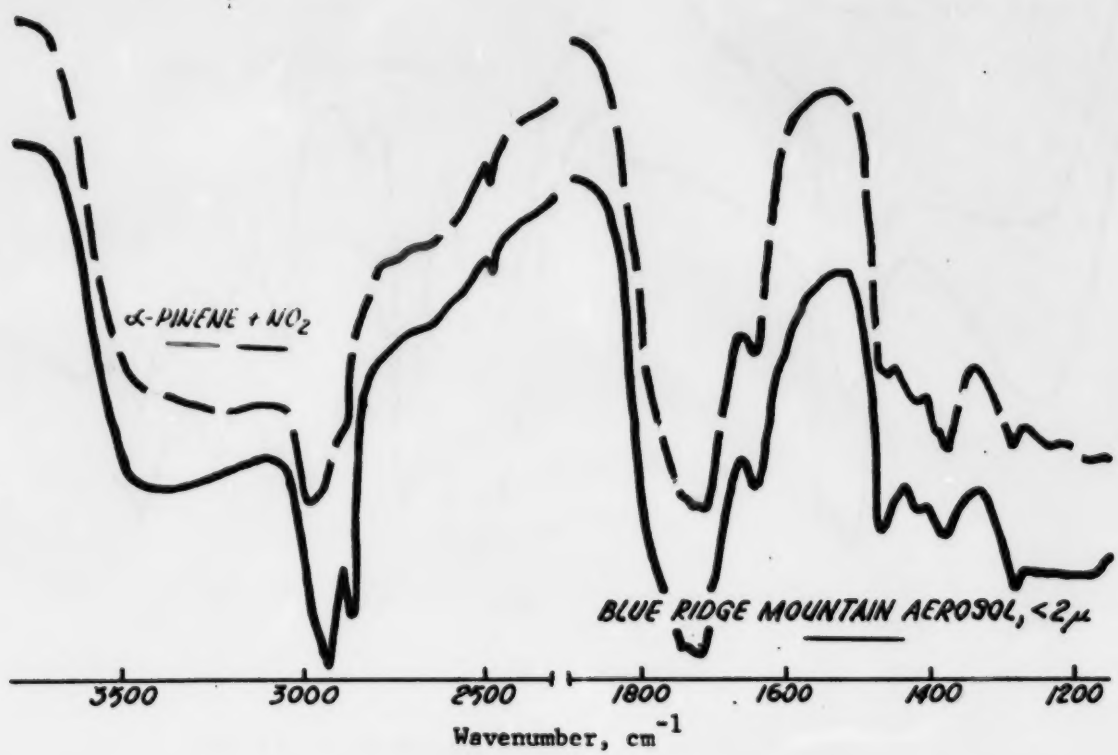


FIGURE 10. COMPARATIVE INFRARED ABSORPTION BANDS OF AEROSOLS GENERATED IN A SMOG CHAMBER FROM A MIXTURE OF A PURE TERPENE (α-PINENE) WITH NO_x AND IN A NATURAL FORESTED ATMOSPHERE (BLUE RIDGE MOUNTAINS)

absorption, and the increase in organic acid OH, C=O, and NO_2 or C=O absorption in the photochemical aerosol can be seen. Unfortunately the resolution in the spectra of samples held on filters is low and there do not appear to be any characteristic absorptions that can be used to differentiate primary and secondary aerosols from automobiles.

In Figures 9 and 10 are shown portions of the infrared spectra obtained by extracting the aerosol material with methylene chloride and evaporating the solution to dryness on a sodium chloride plate. Considerably better resolution is obtained in the 6-micron region. The C=O peaks have been observed and commented on previously[5] but the identification of the 6.2-micron peak with C=C and organic nitrates is believed to be new. This assignment has been supported by the observation, with gas chromatography-mass spectroscopic techniques, of unsaturated organic acids in aerosols formed from 1-heptene/NO_x and a nitrate ester in the aerosols formed from cyclohexene/NO_x.

In Figure 9, the spectra of aerosols from 1-heptene/NO_x and from atmospheric aerosols collected at the Cooper-Union site are compared. In Figure 10, a similar comparison from α-pinene/NO_x, and the Blue Ridge Mountains aerosol is shown. The similarities are quite evident, the major differences being in the height of the nitrate or C=C peaks. The series of absorptions between 8-12 microns have not been identified.

Analysis of Particulate Extracts: Sample Sources and Analytical Objectives

Organic extracts of particulate from the following sources were prepared:

(1) Urban and rural atmospheric haze

(2) Primary auto exhaust

(3) Aerosol generated from known precursors in Battelle-Columbus' smog chamber.

---

(5) Renzetti, N. A., and Doyle, G. J., "The Chemical Nature of the Particulate in Irradiated Auto Exhaust", JAPCA, 8, 293 (1959).

Urban air particulate was collected at the Cooper-Union sampling site during the periods 9/23/70 through 9/26/70 and 9/29/70 through 10/1/70. The 4-day period beginning 9/23/70 was extremely hot and clear and was marked by fairly intensive photochemical smog episodes as evidenced by the oxidant levels shown in Figure 11. For comparison, the maximum hourly average total oxidant measured at this site between July 20 and October 1 exceeded 10 pphm on only 3 days (measurements made by the New York Air Resources Laboratory). Following two days of rain, the period beginning 9/29/70 was quite cool and cloudy and very little photochemical smog was evident. Visibility during the collection periods is indicated in Figure 1. A conventional hi-vol sampler was used to collect aerosols at the Cooper-Union site. Facilities were not available there to measure total sampling size or total particle mass.

Rural-air particulate was collected with both a 2-stage cyclone sampler and a conventional hi-vol sampler. The particulate analyzed was collected exclusively with the cyclone-equipped sampler during clear weather in the period 1/18/70 through 10/23/70. On one day in that period (10/20/70) it rained. During clear weather a blue-grey haze was noticeable in the daytime. The air flow rate through the conventional sampler averaged 16 cfm; that through the cyclone sampler averaged 14 cfm. The particulate mass concentration averaged 31 $\mu g/m^3$ with the conventional sampler; 26 $\mu g/m^3$ with the cyclone sampler. On this basis it appears that the diameters of aerosols associated with forested areas are predominantly in the light-scattering size range or smaller.

Primary auto-exhaust particulate was generated from a 1967 automobile operating on a chassis dynamometer. The method of sample collection was described earlier.

Initial analytical studies were concerned with defining general similarities and differences between urban air particulate and primary auto exhaust particulate. Particulate matter from the two sources was fractionated into organic acid, basic, and neutral classes; the general distribution of material with respect to organic chemical class was thus determined. Subsequent work involved infrared spectroscopic, gas chromatographic, and mass spectral analysis of various components of the

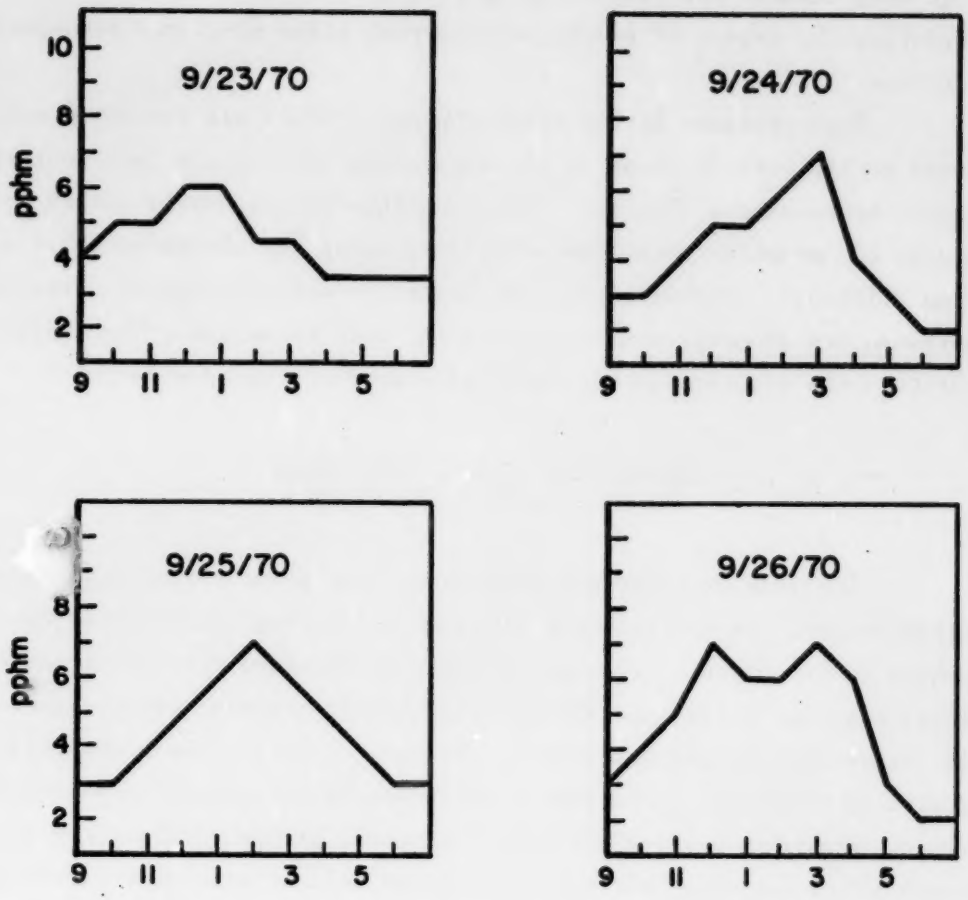


FIGURE 11. HOURLY AVERAGE PLOTS OF TOTAL OXIDANTS, COPPER-UNION SITE, NEW YORK CITY

particulate matter. Specifically, auto exhaust components were sought that could be utilized as "fingerprint" compounds to establish the contribution of auto exhaust to atmospheric pollution.

Several components of aerosol produced in the smog chamber from known precursors were identified by mass spectral techniques. These analyses of smog chamber reaction products were conducted with the objective of elucidating the nature of reactions occurring under simulated atmospheric conditions.

High-pressure liquid chromatography (HPLC) was evaluated with respect to its effectiveness in the separation and assay of polynuclear aromatic hydrocarbons (PNA's). This technique is especially suited to the analysis of compounds whose low volatility makes gas chromatographic separation difficult. Further, HPLC is compatible with the use of ultraviolet absorbence and fluorescence techniques for peak detection. The utility of HPLC in the chromatographic separation of PNA's was demonstrated.

Comparison of Air Particulate and Auto Exhaust Particulate

Analysis of urban air particulate and primary auto exhaust was undertaken with the general objective of elucidating similarities and differences in the organic fraction of material obtained from these sources. Initial analyses determined the distribution of material among organic acid, basic and neutral fractions. The above fractions were analyzed by infrared spectroscopy to determine the presence and approximate concentrations of compounds bearing specific functional groups. Subsequent study of both urban and rural air particulate, as well as auto exhaust particulate, involved detailed analysis of the acid fraction of these materials using the techniques of thin-layer chromatography, gas chromatography, and gas chromatography interfaced with mass spectroscopy (GC-MS). It was the objective of this phase of the work to identify specific components of auto exhaust that might be utilized as "fingerprint" compounds to establish the contribution of auto exhaust to atmospheric pollution.

Chemical Fractionation and Infrared Spectroscopic Analysis

The methylene chloride extracts of urban air particulate and auto exhaust particulate were fractionated according to the scheme shown in Figure 12. As indicated, the residues obtained upon removal of methylene chloride by distillation were extracted with redistilled diethyl ether; 79 percent of the air particulate residue went into ether solution, while 85 percent of the auto exhaust residue went into ether solution. Infrared spectroscopy indicates that the aromatic hydrocarbon content is severalfold higher in the ether insoluble fraction than in the ether soluble fraction.

The approximate material distribution among the organic acid, basic, and neutral fractions of air and auto exhaust particulate is shown below.

	Material Distribution		
	Acid Fraction	Basic Fraction	Neutral Fraction
Air particulate	~ 24%	~ 38%	~ 38%
Auto exhaust particulate	~ 26%	~ 16%	~ 58% .

Infrared spectroscopy of the neutral fraction of the above samples reveals the presence of significant concentrations of ester, aldehyde, and ketone in material isolated from air particulate. The ester concentration is greater than that of the combined aldehydes and ketones; the concentrations are in an approximate ratio of (ester):(aldehyde + ketone) $\tilde{=}$ 10:1. Such carbonyl and carboxyl containing compounds are largely absent (i.e., < 5%) from the neutral fraction of auto exhaust particulate. The neutral fraction of auto exhaust particulate is almost entirely hydrocarbon, with an (aliphatic):(aromatic) ratio of approximately 85:15. This is approximately the ratio observed in the hydrocarbon component of urban air particulate.

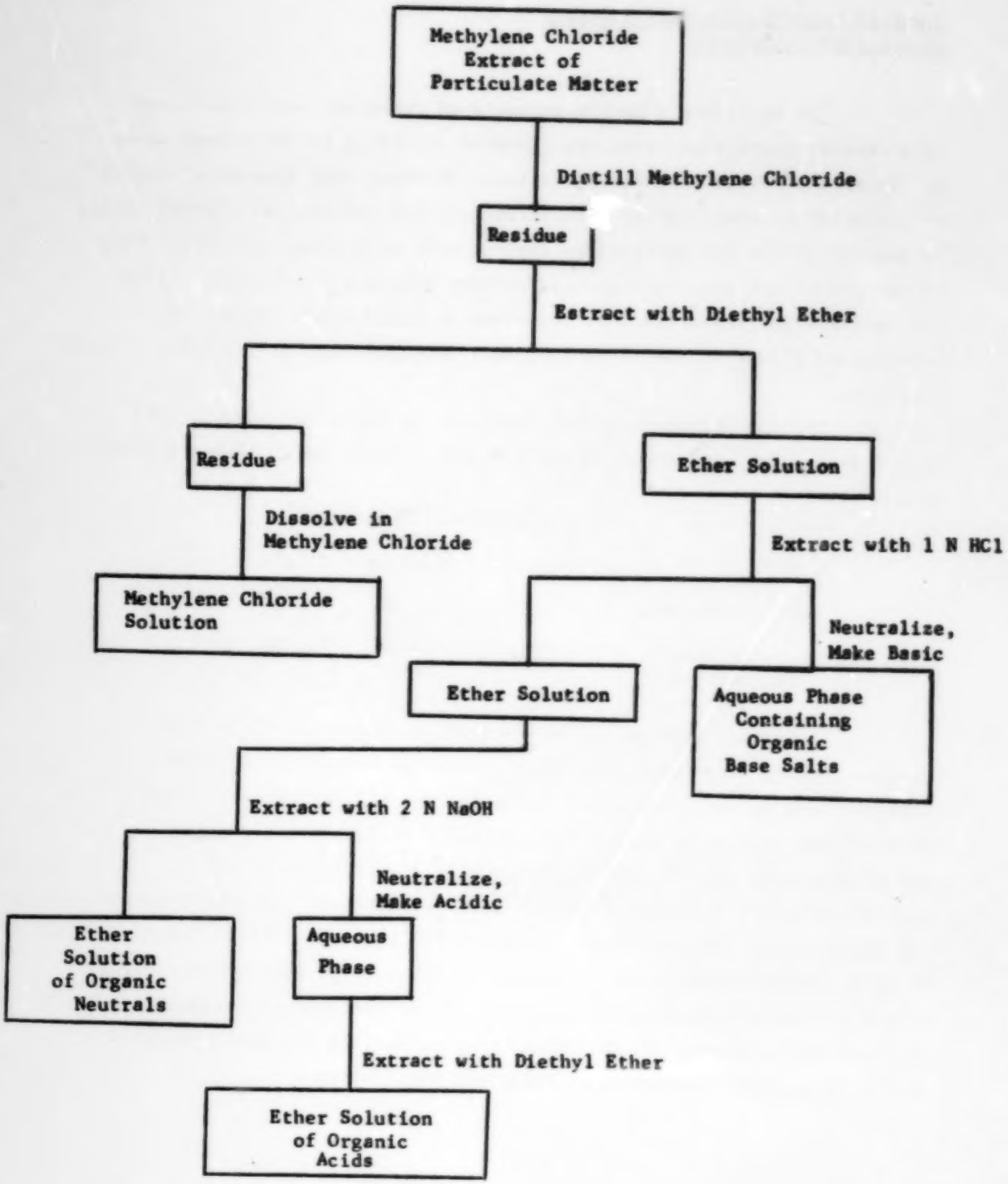
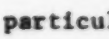


FIGURE 12. SCHEME FOR ORGANIC CLASS-SEPARATION

Isolation of the basic fraction of urban air particulate was attempted by extraction of the ether soluble fraction with 1N HCL. The HCl extract was neutralized, made basic (pH = 13), and extracted with diethyl ether to recover the organic base. Most of the basic material, however, was not recoverable by ether extraction of the aqueous phase. Approximately 38 percent of the total ether soluble fraction went into solution upon extraction with 1 N HCl. However, when the HCl extract was made basic only ~2 percent of the ether soluble material could be recovered. Note in addition that previous extraction of the total ether soluble fraction with distilled water did not indicate the presence of an appreciable water soluble component.

The solubility behavior of this relatively hydrophillic component of the basic fraction tends to indicate that the compounds present are polar in nature and are polyfunctional. The presence of polar functional groups would tend to increase the hydrophillic character of the molecule, rendering recovery of the material by extraction from an aqueous phase more difficult.

Infrared spectroscopy of the ether extractable base revealed the absence of primary, secondary, or tertiary amines. The infrared data tend to indicate the presence of nitrogen containing heterocyclic aromatics such as pyridine or acridine.

Infrared spectroscopy of the acid components of the above samples indicates a greater concentration of alcoholic hydroxy containing compounds (R-OH and ArOH) in the fraction isolated from auto exhaust particulate than that isolated from urban air particulate. That is, the ratio of (): ( ) is several fold higher for auto-exhaust particulate than urban air particulate. The (aromatic):(aliphatic) ratio is approximately 5:95 for air particulate and approximately 75:25 for auto-exhaust particulate.

Analysis by Gas Chromatography and Gas Chromatography Interfaced With Mass Spectrometry

Organic acids isolated from urban and rural air particulate and from primary auto exhaust particulate were analyzed using gas chromatography (GC) and gas chromatography interfaced with mass spectroscopy

(GC-MS). Methyl esters of the acids were prepared by reaction with diazomethane. The products were gas chromatographed, using a 10-ft x 1/8-in. column of 10 percent ethylene glycol succinate (EGS) on Gas Chrom Q, as well as a 10-ft x 1/8-in. column of 3 percent OV-17 on Gas Chrom Q. GC analysis of esterified urban air particulate acids revealed the presence of various long-chain carboxylic acid esters, principally palmitate and stearate with lesser concentrations of laurate, myristate and arachidate. Initial peak assignments were made on the basis of comparative retention times using authentic samples of the various methyl esters. The presence of methyl palmitate and methyl stearate was confirmed by GC-MS. Several other tentatively identified ester peaks did not produce discernible parent-ion peaks (GS-MS), but did produce fragmentation patterns characteristic of carboxylic acid methyl esters. Similar gas chromatographic analysis of material isolated from auto-exhaust particulate revealed a far lower concentration (~10%) of long-chain carboxylic acid esters than that observed in urban air particulate. On the basis of gas chromatographic retention times, lauric, myriatic, palmitic, and stearic acid esters can be tentatively identified. Gas chromatographic analysis of acids isolated from rural air particulate associated with natural haze similarly revealed a carboxylic acid concentration lower than that found in urban air particulate. Lauric, palmitic, and stearic acid esters can be tentatively identified on the basis of gas chromatographic retention times. Subsequent analysis of natural haze acids by GC-MS confirmed the presence of methyl palmitate and also revealed the presence of methyl pinonate. Pinonic acid is an oxidation product of α-pinene, a natural terpene present in forest atmosphere. This finding is discussed in detail in the report section dealing with analysis of smog-chamber aerosol generated from α-pinene.

Comparison of the above gas chromatograms indicated the presence of materials in the auto-exhaust particulate which were absent (or present in negligible concentration) in air particulate. To simplify gas chromatographic analysis of the complex mixtures of acids, the esterified samples were fractionated by preparative thin-layer

chromatography (TLC) on silica gel. Plates were developed with chloroform and visualized using ultraviolet illumination. The various TLC fractions were analyzed gas chromatographically. A principal difference between auto exhaust and air particulate was noted in the gas chromatogram of TLC fraction No. r (rt = 0.35 - 0.70). Two major peaks in the chromatogram of auto-exhaust material were absent in that of air-particulate material (see Figures 13 and 14). Mass spectroscopy was performed to characterize the two compounds in question. The mass spectra are unambiguous and establish the two peaks as corresponding to methyl benzoate (Peak A) and methyl phenylacetate (Peak B). The mass spectra are shown in Figures 15 and 16.

Compounds such as the two identified above could possibly be utilized as "fingerprint" compounds to establish the contribution of primary auto exhaust to atmospheric pollution. Air- and auto-exhaust particulate samples from a variety of other sources should be analyzed to confirm the feasibility and reliability of such "fingerprint" utilization in procedures to establish automotive contribution to atmospheric pollution.

Analysis of Smog Chamber Aerosol

A variety of pure compounds were reacted in Battelle's smog chamber. Concentrations of reactants employed, the smog chamber operating conditions, and smog parameters are described in Table 1. Analyses of reaction products generated were conducted with the objective of elucidating the nature of reactions occurring under such simulated atmospheric conditions. In view of the oxidizing conditions that obtain under such conditions, the acid (most oxidized) fraction of reaction products was isolated for analysis by gas chromatography and mass spectroscopy.

Typically, the acid fraction was isolated by extraction of the total methylene chloride extract with 2N NaOH. The basic aqueous extract was then reacidified to pH $\sim$ 1.5 and extracted with methylene chloride. The methylene chloride solution was dried over anhydrous $MgSO_4$ and the solvent was removed by distillation. A portion of the isolated acid was esterified with diazomethane and the methyl esters produced were analyzed using gas chromatography and gas chromatography interfaced with mass spectroscopy (GC-MS).

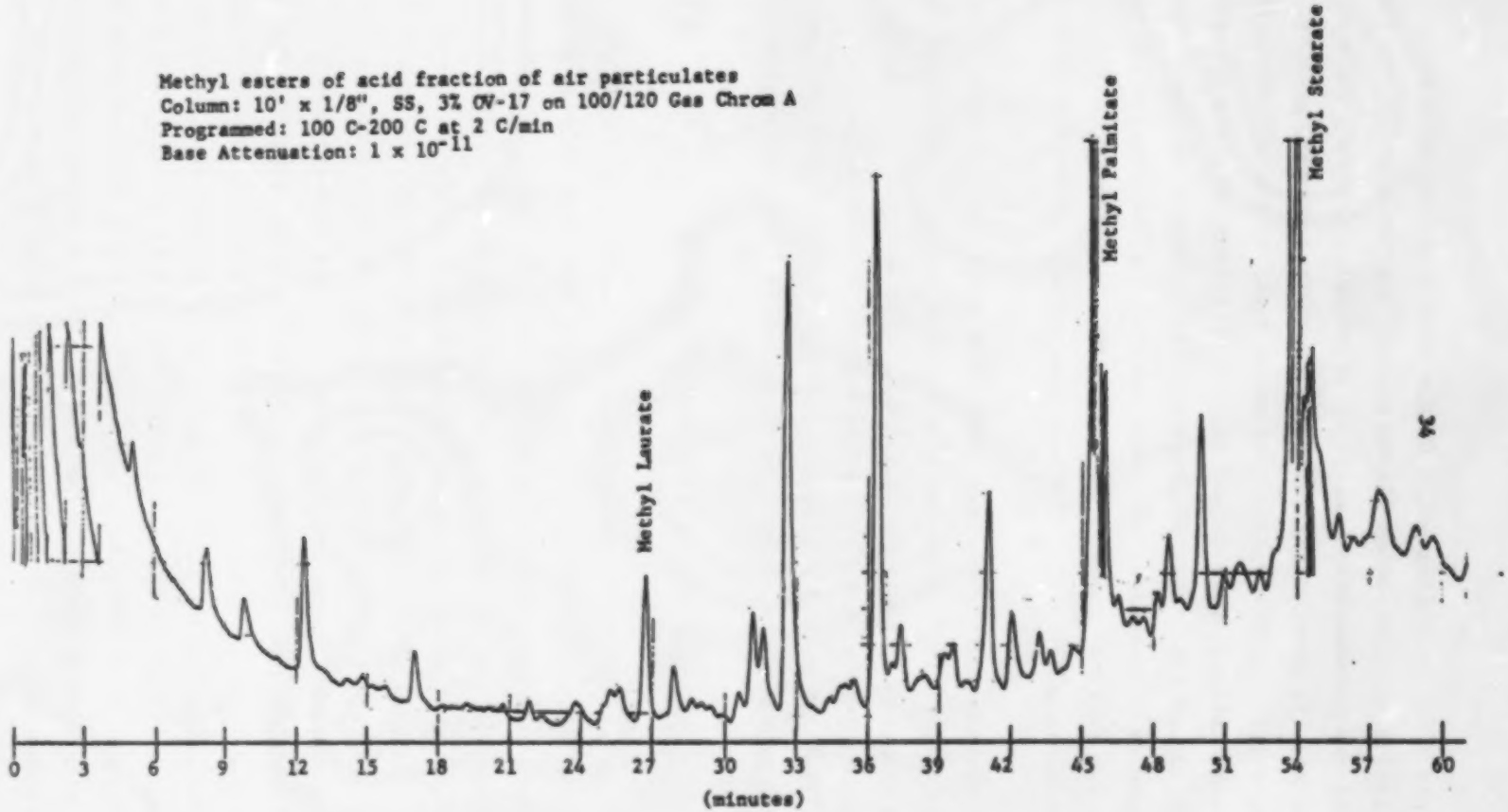


FIGURE 13. GAS CHROMATOGRAM OF METHYL ESTERS OF ACID FRACTION ISOLATED FROM AIR PARTICULATE

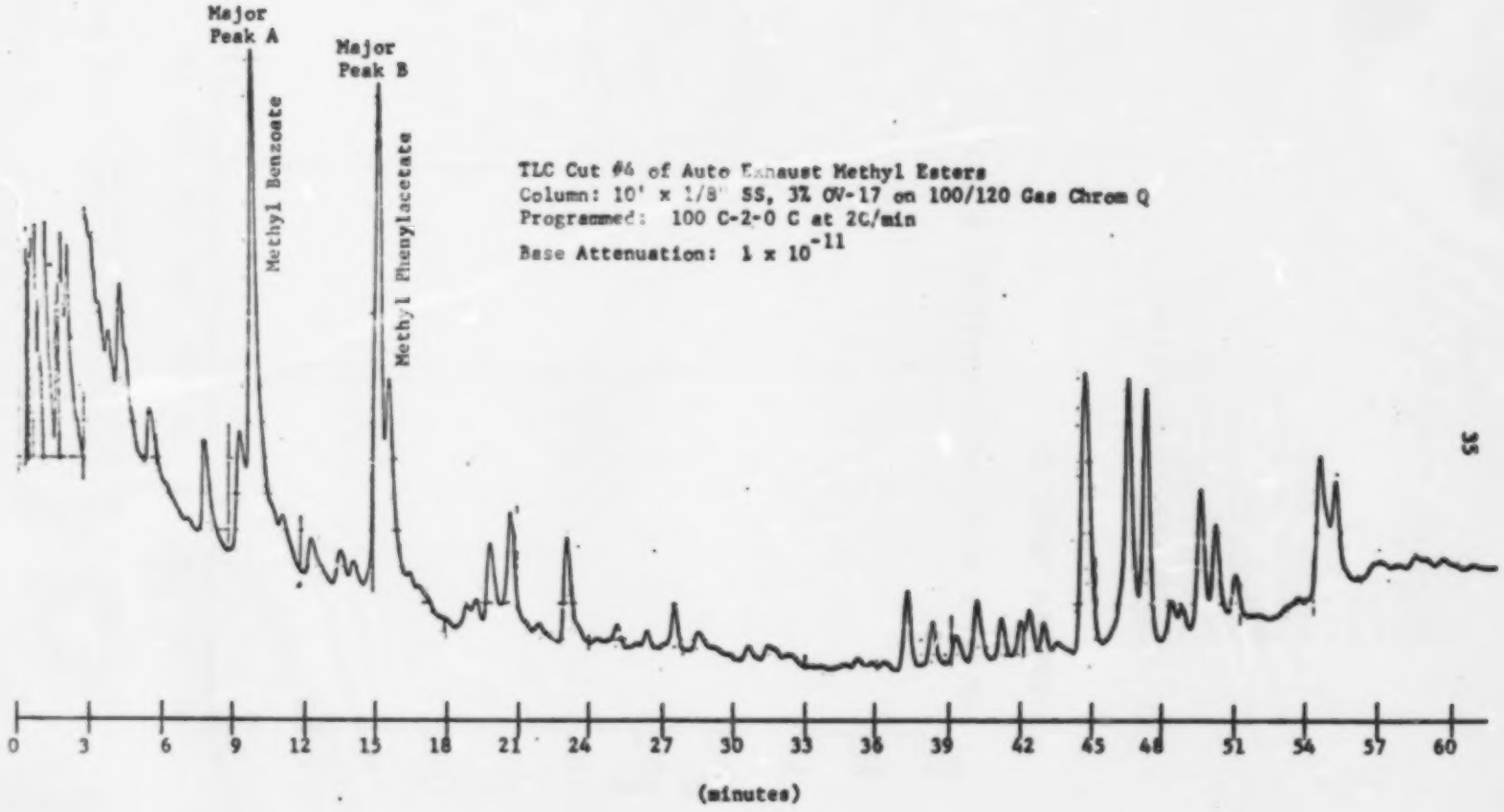

Major
Peak A
Major
Peak B
Methyl Benzoate
Methyl Phenylacetate
TLC Cut #4 of Auto Exhaust Methyl Esters
Column: 10' x 1/8" SS, 3% OV-17 on 100/120 Gas Chrom Q
Programmed: 100 C-2-0 C at 2C/min
Base Attenuation: 1 x 10^-11
35
0 3 6 9 12 15 18 21 24 27 30 33 36 39 42 45 48 51 54 57 60
(minutes)

FIGURE 14. GAS CHROMATOGRAM OF TLC FRACTIONATED METHYL ESTERS OF ACID FRACTION ISOLATED FROM AUTO EXHAUST PARTICULATE

```
SYSTEM 158 IS ON
SELECT MODE:  OUTP
PRINT?:
PLOT?:  Y
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AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?:  Y
BACKGROUND FILE NAME:  13-2
SPECTRUM NUMBER:  28
BACKGROUND AMPLIFICATION:
NORMALIZE ON:
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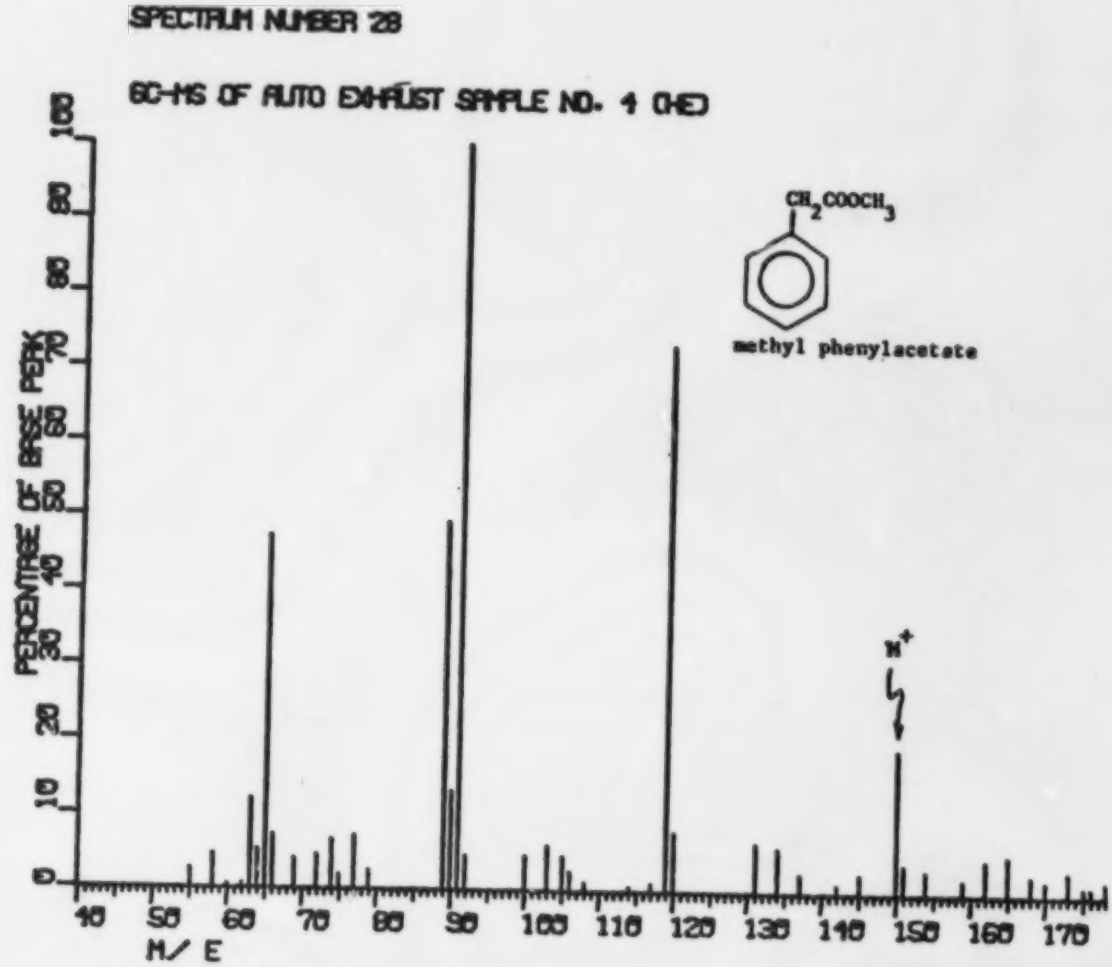

FIGURE 15. MASS SPECTRUM OF MAJOR PEAK B IN GAS CHROMATOGRAM OF AUTO EXHAUST METHYL ESTERS

```
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PRINT?:
PLOT?:  Y
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SPECTRUM NUMBER:  10
AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?: Y
BACKGROUND FILE NAME: 13-2
SPECTRUM NUMBER:  5
BACKGROUND AMPLIFICATION:
NORMALIZE ON:
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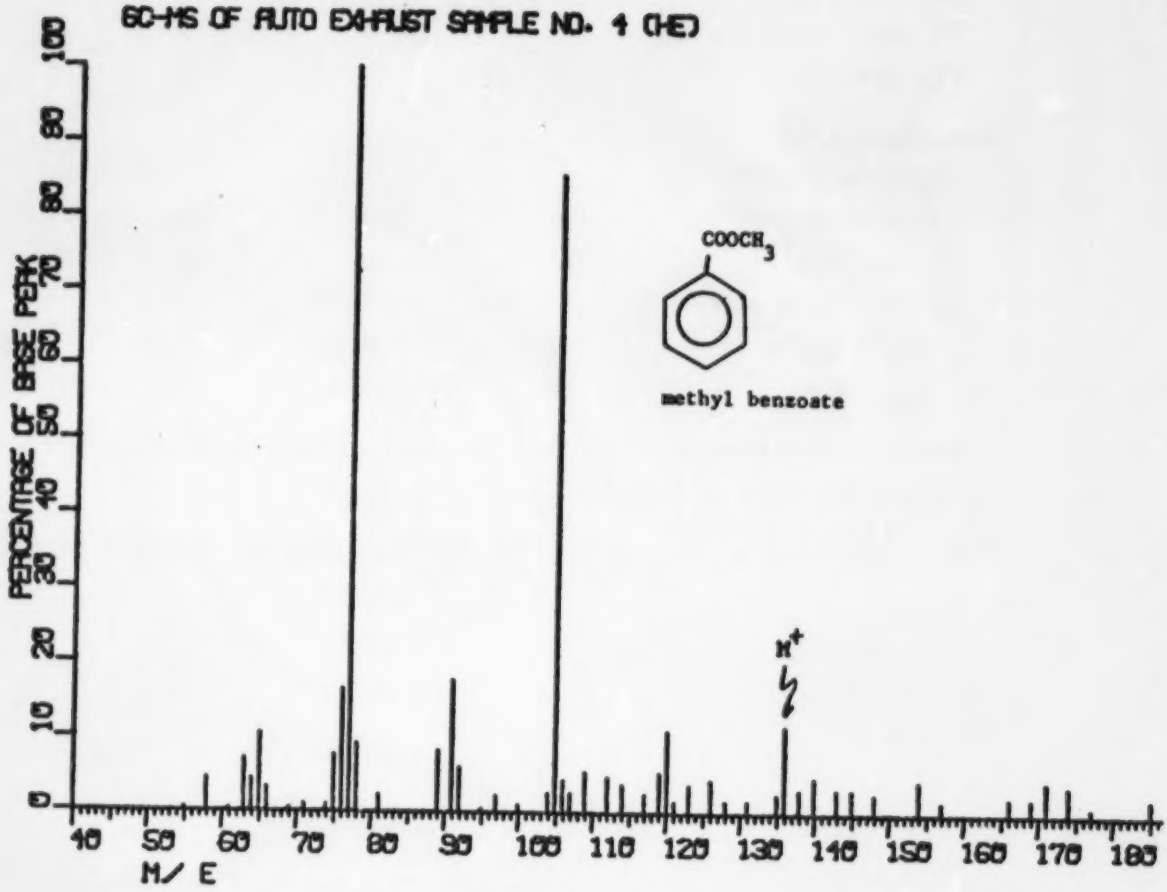


FIGURE 16. MASS SPECTRUM OF MAJOR PEAK A IN GAS CHROMATOGRAM OF AUTO EXHAUST METHYL ESTERS

TABLE 1. SUMMARY OF PURE HYDROCARBON RUNS IN 610-CU-FT SMOG CHAMBER

Hydrocarbon	α-Pinene	Cyclohexene	1-Heptene	Toluene
Initial Conditions				
Temperature, F	88	90	90	89
RH, percent	41	39	41	43
HC, ppm[(a)]	10	10	10	10
NO, ppm	1	0	1	1
NO_2, ppm	1	2	1	1
Smog Parameters				
Light scattering				
b-scat max, $10^{-4}m^{-1}$	190	214	126	73
t-max, min[(b)]	10	18	80	150
Oxidant (Mast meter)				
C-max, ppm as O_3	0.25	0.32	0.79	0.60
t_{max}, min	8	15	75	115

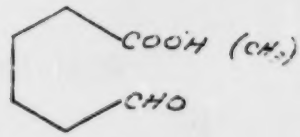
(a) All ppm units are vol/vol.

(b) Aerosol collections made after light-scattering reached a maximum.

Aerosol Generated from Cyclohexene

The aerosol generated from cyclohexene was collected and the organic acid isolated according to procedures described above. A portion of the isolated acid was treated with diazomethane and the resulting methyl esters were analyzed by GC-MS. The reconstructed gas chromatogram is shown in Figure 17. Several tentative identifications can be made on the basis of mass spectra of the indicated chromatographic peaks.

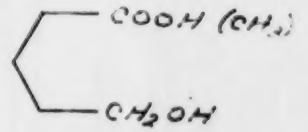
(1) Major peak C can be tentatively identified as the methyl ester of the difunctional aldehydo-acid:



(I)

The mass spectrum is shown in Figure 18.

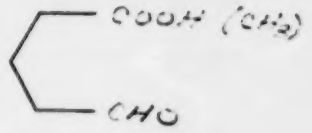
(2) Major peak B can be tentatively identified as the methyl ester of 5-hydroxypentanoic acid:



(II)

The mass spectrum is shown in Figure 19.

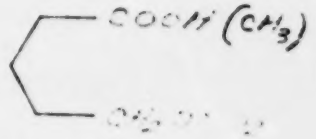
(3) Major peak A can be tentatively identified as the methyl ester of the difunctional aldehydo-acid:



(III)

The mass spectrum is shown in Figure 20.

(4) Major peak D can be tentatively identified as the nitrate ester of the above methyl 5-hydroxypentenoate:



(IV)

The mass spectrum is shown in Figure 21. Recall that the cyclohexene was reacted in the smog chamber in the presence of NO_2.

```
SYSTEM 150 IS ON          40
SELECT MODE:  IFSS
CALIBRATE?:
TITLE:  GC-MS (CH4) OF CYCLOHEXANE-NO2 PRODUCTS
CALIBRATION FILE NAME:  CAL-H  A
FILE NAME:  24-3
MASS RANGE:  50-350
SAMPLES/AMU:  1
MAX RPT COUNT:  4
BASE INTEGRATION TIME:  8
RPT COUNT BEFORE CHECKING LOWER THRESHOLD:  4
LOWER THRESHOLD:  3
UPPER THRESHOLD:  4
1015 RANGE SETTING?:  H
MAX RUN TIME:  30
```

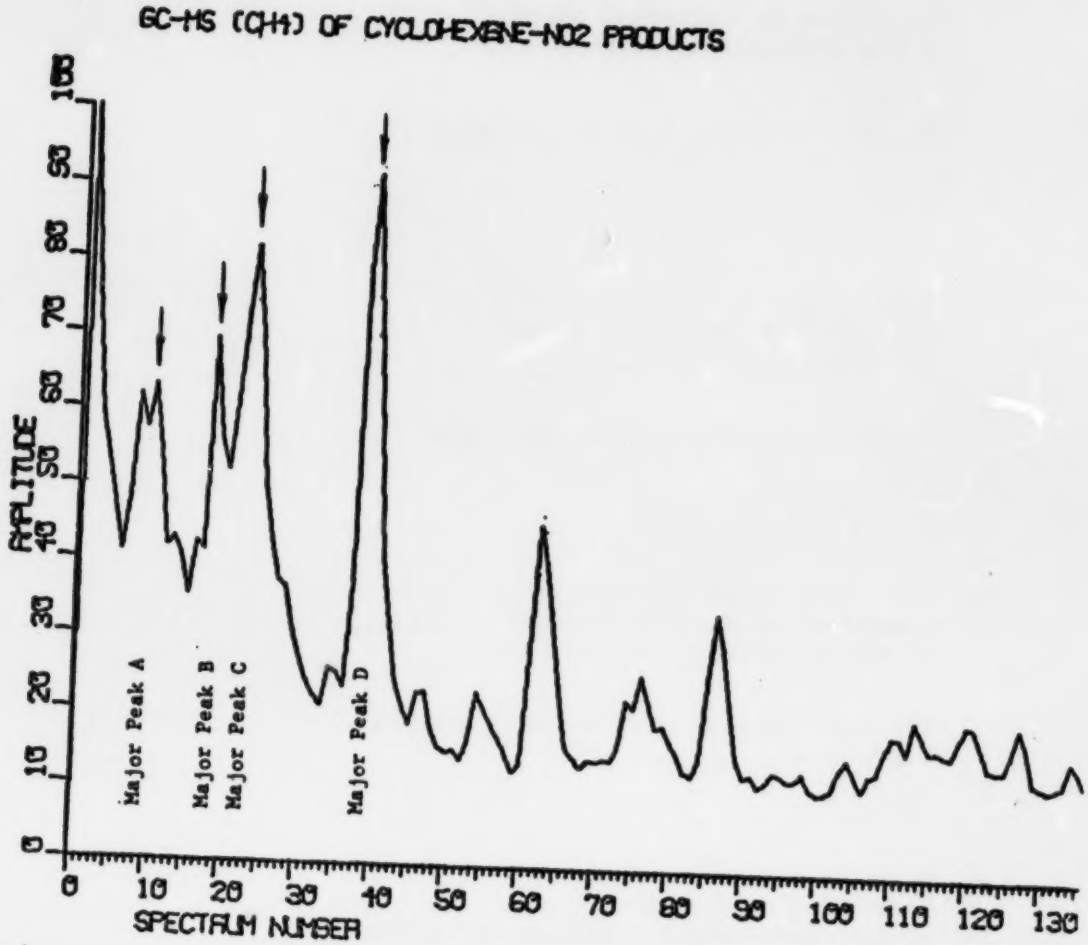


FIGURE 17. RECONSTRUCTED GAS CHROMATOGRAM OF CYCLOHEXENE REACTION PRODUCTS

```
SYSTEM 150 IS ON
SELECT MODE:  OUTP
PRINT?:
PLOT?:  Y
FILE NAME:  24-3
SPECTRUM NUMBER:  23
AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?:  Y
BACKGROUND FILE NAME:  24-3
SPECTRUM NUMBER:  20
BACKGROUND AMPLIFICATION:
NORMALIZE ON:
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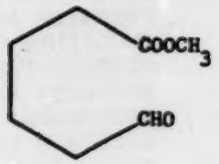
Tentative assignment:



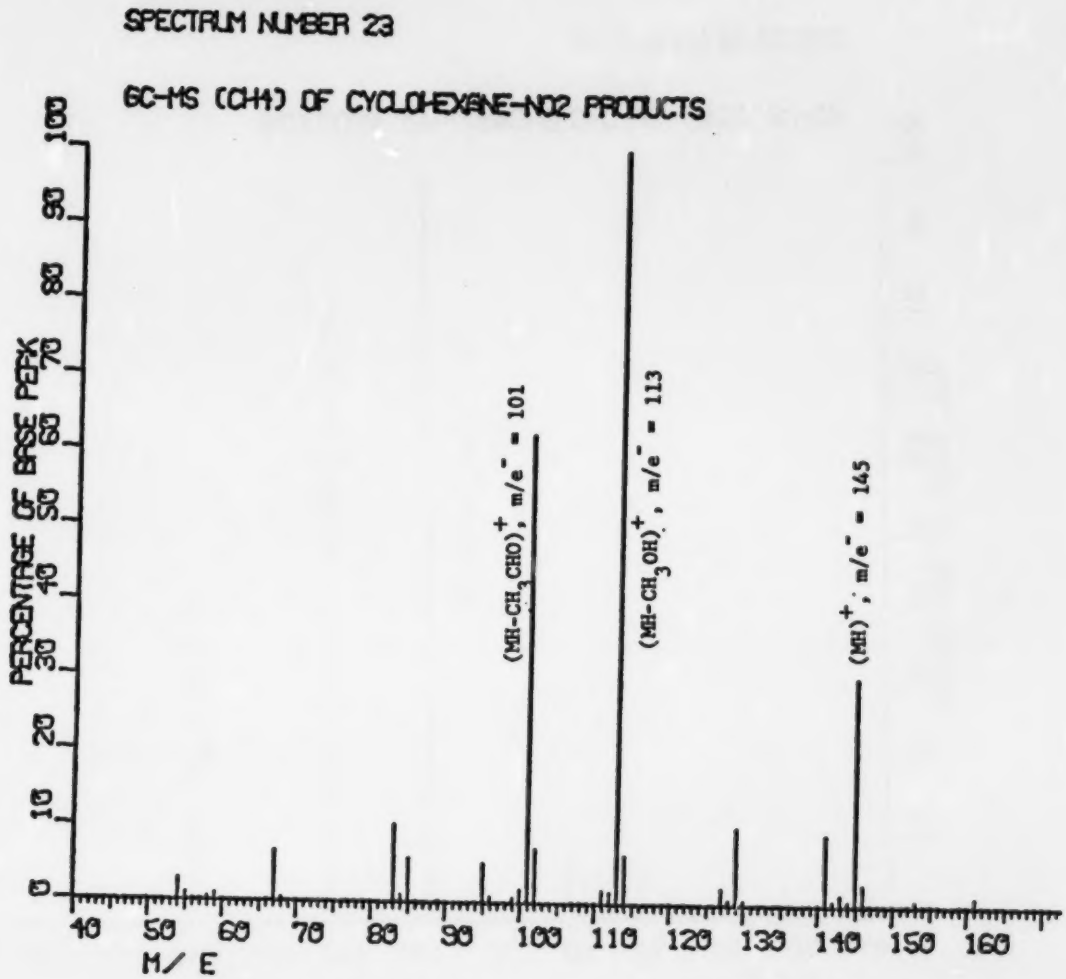


FIGURE 18. ANALYSIS OF CYCLOHEXENE REACTION PRODUCTS: CHEMICAL IONIZATION MASS SPECTRUM FOR GAS CHROMATOGRAPHIC PEAK (C)

(Refer to Figure 17)

```
SYSTEM 150 IS ON
SELECT MODE:  OUTP
PRINT?:
PLOT?:  Y
FILE NAME:  24-3
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AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?:  Y
BACKGROUND FILE NAME:  24-3
SPECTRUM NUMBER:  15
BACKGROUND AMPLIFICATION:
NORMALIZE ON:
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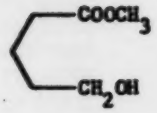
Tentative assignment:



SPECTRUM NUMBER 18

GC-MS (CH4) OF CYCLOHEXENE-NO2 PRODUCTS

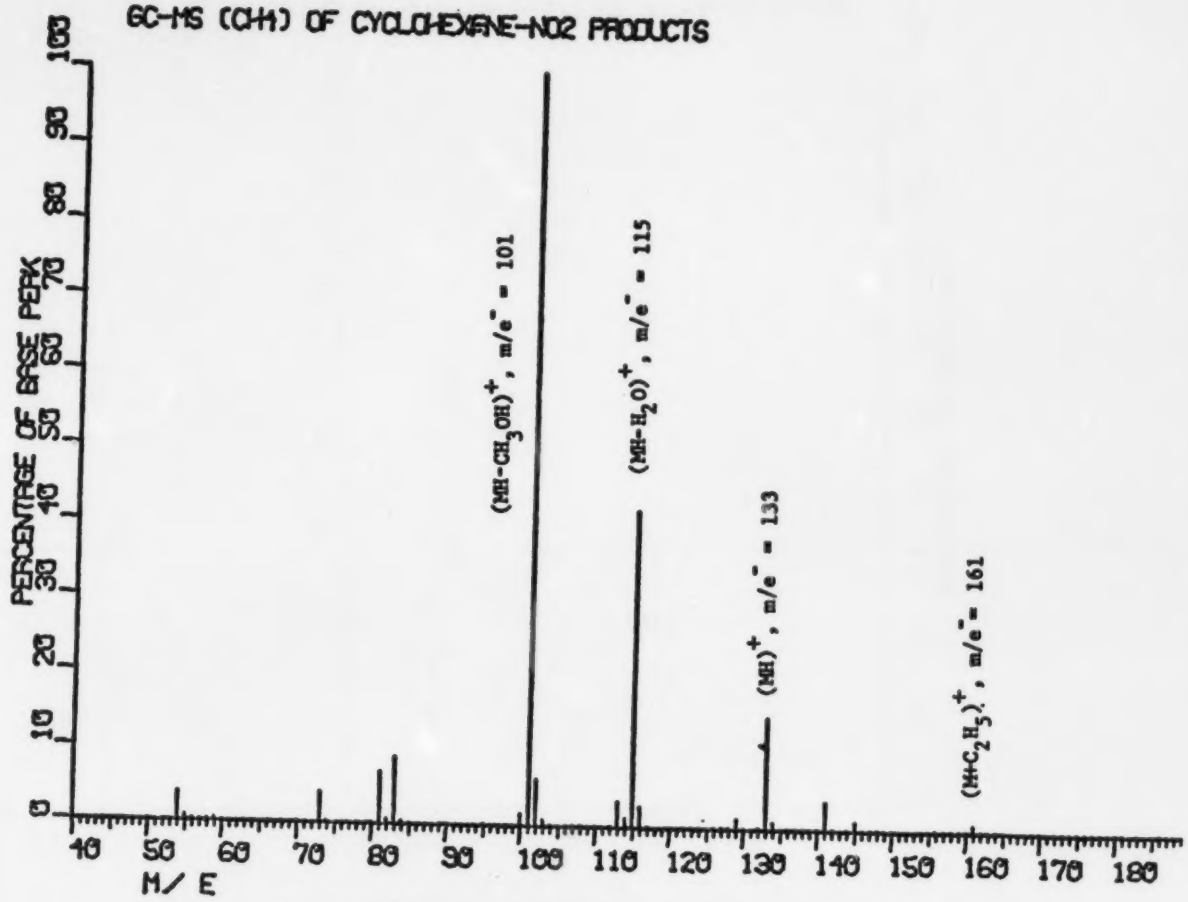


FIGURE 19. ANALYSIS OF CYCLOHEXENE REACTION PRODUCTS: CHEMICAL IONIZATION MASS SPECTRUM FOR GAS CHROMATOGRAPHIC PEAK (B) (Refer to Figure 17)

```
SYSTEM 150 IS ON
SELECT MODE:  OUTP
PRINT?:
PLOT?:  Y
FILE NAME:  24-3
SPECTRUM NUMBER:  10
AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?:  Y
BACKGROUND FILE NAME:  24-3
SPECTRUM NUMBER:  6
BACKGROUND AMPLIFICATION:
NORMALIZE ON:
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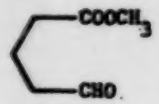
Tentative assignment:



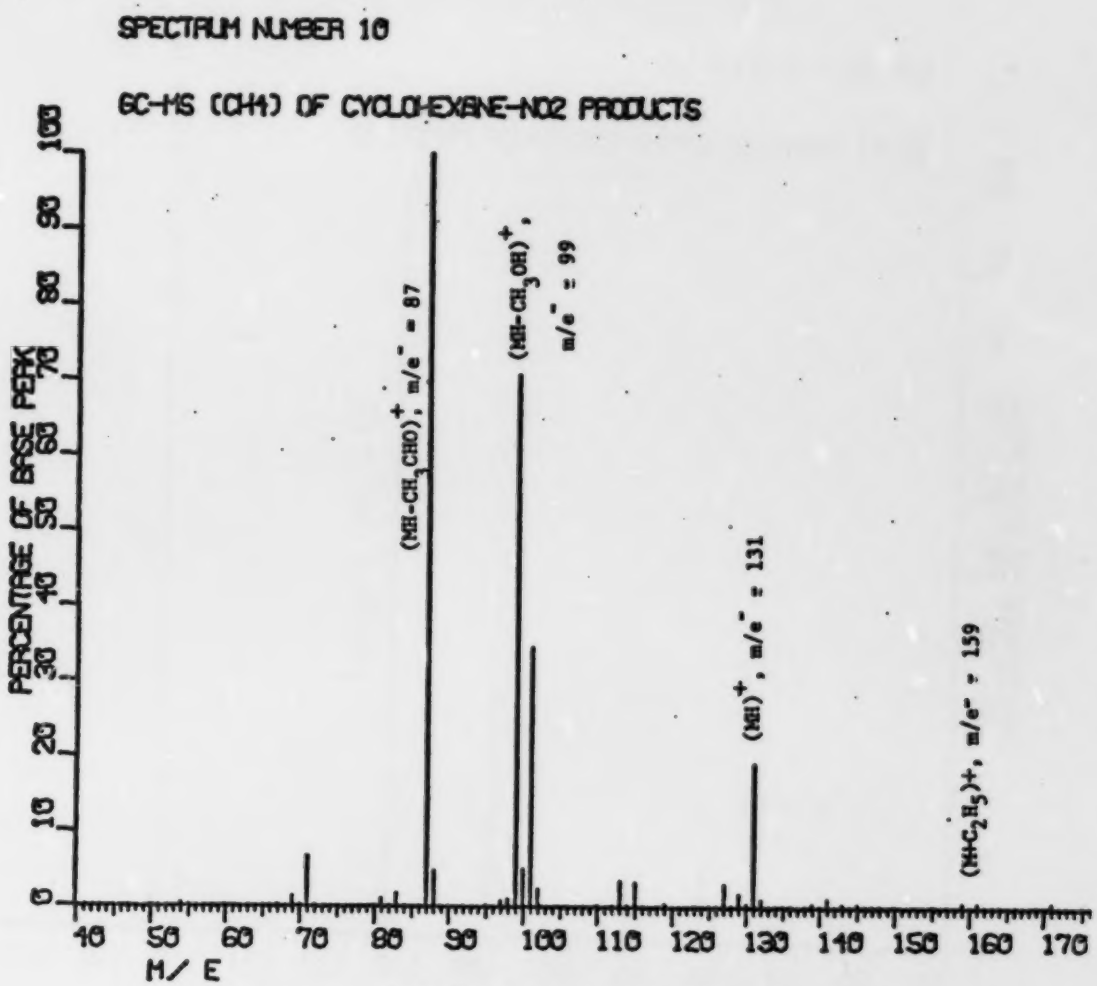
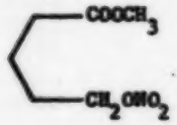


FIGURE 20. ANALYSIS OF CYCLOHEXENE REACTION PRODUCTS: CHEMICAL IONIZATION MASS SPECTRUM FOR GAS CHROMATOGRAPHIC PEAK (A)

(Refer to Figure 17)

SYSTEM 150 IS ON
SELECT MODE: OUTP
PRINT?:
PLOT?: Y
FILE NAME: 84-3
SPECTRUM NUMBER: 39
AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?: Y
BACKGROUND FILE NAME: 84-3
SPECTRUM NUMBER: 36
BACKGROUND AMPLIFICATION:
NORMALIZE ON:

Tentative assignment:



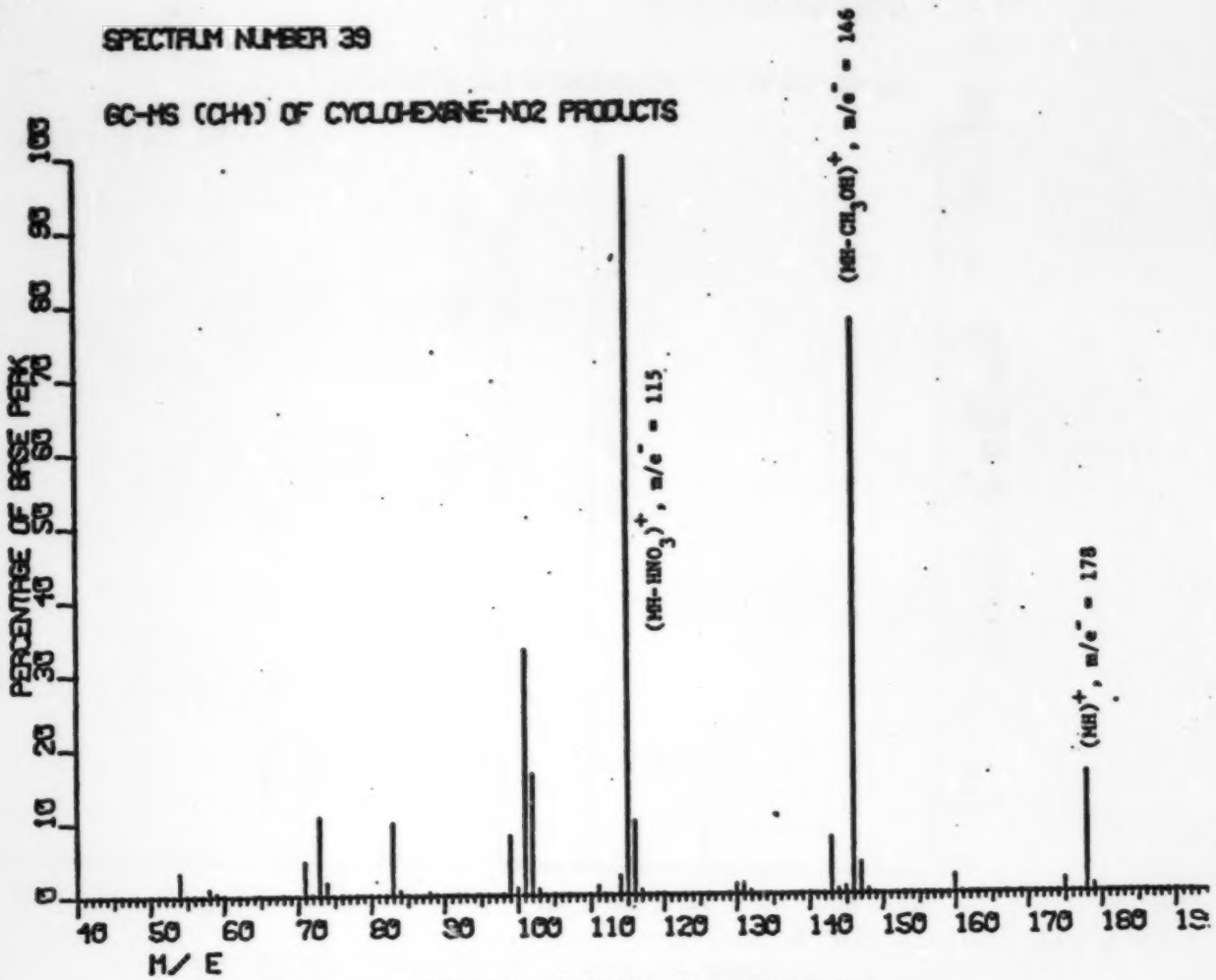


FIGURE 21. ANALYSIS OF CYCLOHEXENE REACTION PRODUCTS: CHEMICAL IONIZATION MASS SPECTRUM FOR GAS CHROMATOGRAPHIC PEAK (D)

(Refer to Figure 17)

Oxidative cleavage of cyclohexene in the presence of ozone and H_2O_2[6] can reasonably be seen to yield compound (I). Decarboxylation of (I) might yield a dialdehyde OHC-$(CH_2)_3$-CHO which might then undergo disproportionation of yield (II). Alternatively, Compound (I) might be degraded at the aldehyde terminal to yield the hydroxypentanoic acid via an unspecified free radical mechanism. Oxidation of the hydroxy terminal of 5-hydrosypentaboic acid (II) yields the five membered aldehydo-acid, (III).

In summary, several acidic reaction products of cyclohexene have been isolated from smog chamber aerosol and tentatively identified.

Aerosol Generated from α-Pinene

α-pinene, a natural terpene, is produced in large quantities by plants and trees. Significant concentrations of this fragrant volatile compound can be found in the forest atmosphere. The aerosol produced in the smog chamber from this compound was collected, and the acid fraction was isolated as described above. Methyl esters were prepared and analyzed by GC-MS. The reconstructed gas chromotogram is shown in Figure 22. The mass spectrum of the indicated chromatographic peak corresponding to methyl pinonate is shown in Figure 23. This peak can be unequivocally identified as that corresponding to methyl pinonote on the basis of comparison of its mass spectrum with that of authentic methyl-cis-pinonote shown in Figure 24. The mass spectral fragmentation pattern for this compound is rationalized in Table 2.

A second analysis of the sample by GC-MS verified the presence of pinonic acid. The analytical results indicated, in addition, that

---

(6) B. W. Gay and J. J. Bufalini, "Hydrogen Peroxide in the Urban Atmosphere", paper presented at 161st ACS National Meeting, Los Angeles, March, 1971. Hydrogen peroxide was found in irradiated mixtures of hydrocarbons and nitrogen oxides as well as in urban atmosphere during periods of photochemical smog formation.

```
SYSTEM 150 IS ON                    46
SELECT MODE:  IFSS
CALIBRATE?:
TITLE:  GC-MS (CH4) OF METHYL ESTERS FROM PINENE REACTION
CALIBRATION FILE NAME:  CAL-M
FILE NAME:  15-7
MASS RANGE: 50-250
SAMPLES/AMU:  1
MAX RPT COUNT:  4
BASE INTEGRATION TIME:  8
RPT COUNT BEFORE CHECKING LOWER THRESHOLD:  2
LOWER THRESHOLD:  3
UPPER THRESHOLD:  4
1015 RANGE SETTING?:  M
MAX RUN TIME: 30

DATA
```

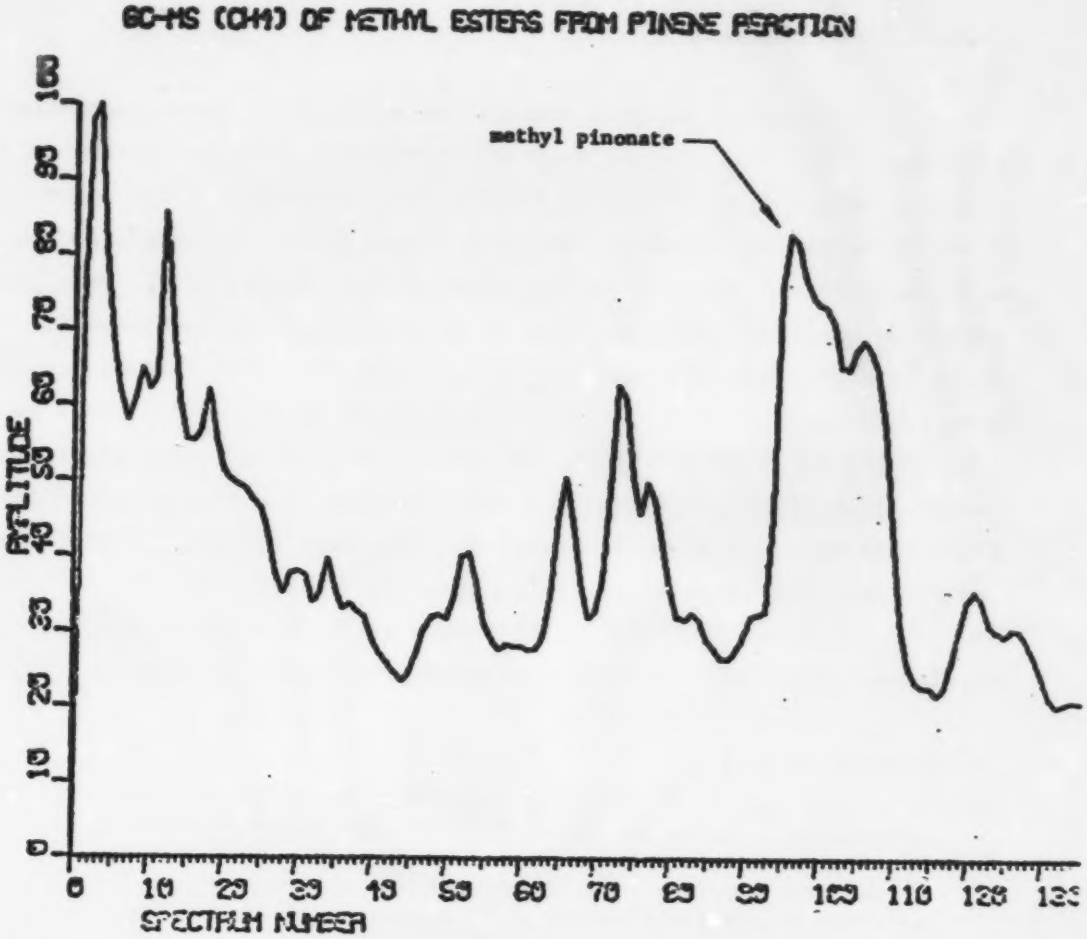


FIGURE 22. RECONSTRUCTED GAS CHROMATOGRAM OF α-PINENE REACTION PRODUCTS

(First Analysis)

```
SYSTEM 150 IS ON
SELECT MODE:  OUTP
PRINT?:
PLOT?:  Y
FILE NAME:  15-7
SPECTRUM NUMBER:  96
AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?:  Y
BACKGROUND FILE NAME:  15-7
SPECTRUM NUMBER:  92
BACKGROUND AMPLIFICATION:
NORMALIZE ON:
```

SPECTRUM NUMBER 96

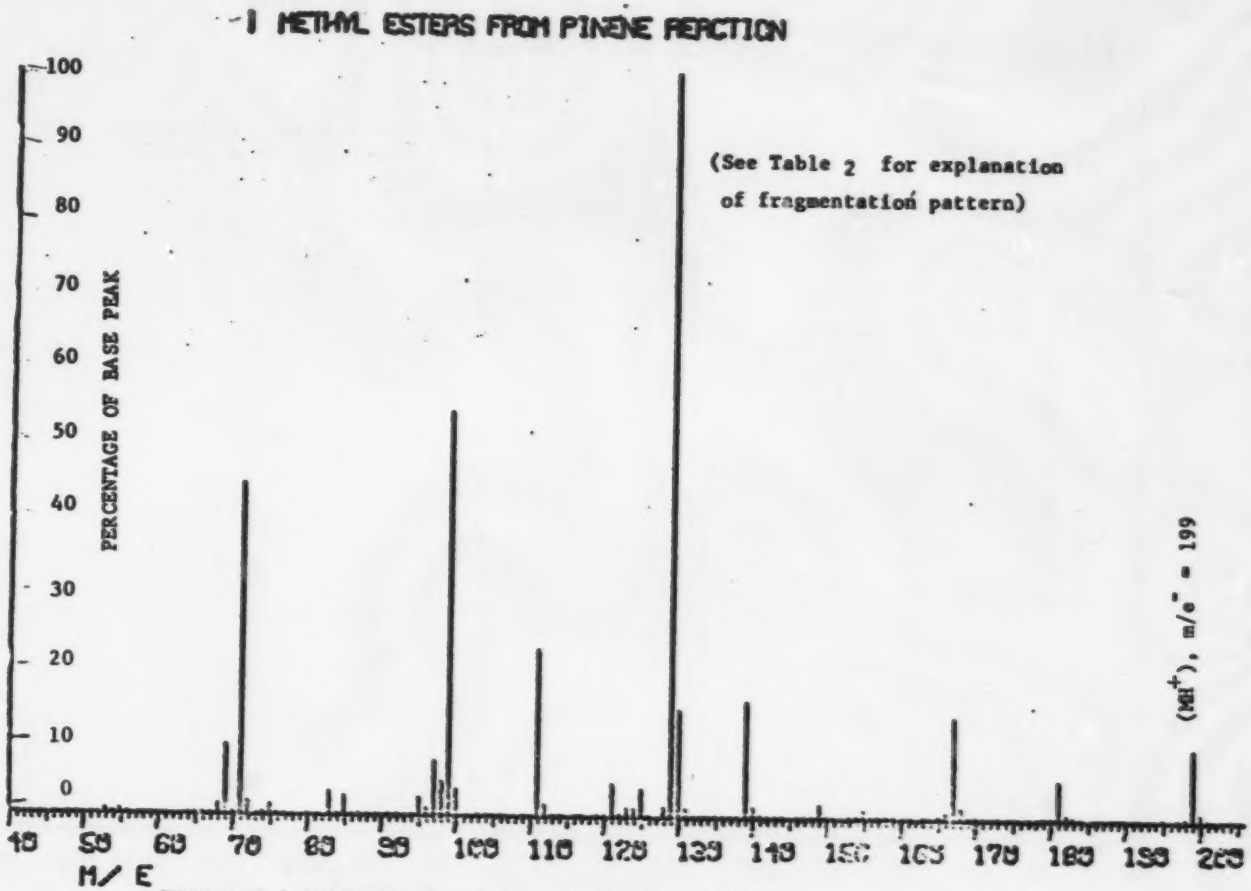


FIGURE 23. ANALYSIS OF α-PINENE REACTION PRODUCTS: CHEMICAL IONIZATION MASS SPECTRUM OF GAS CHROMATOGRAPHIC PEAK CORRESPONDING TO METHYL PINONATE

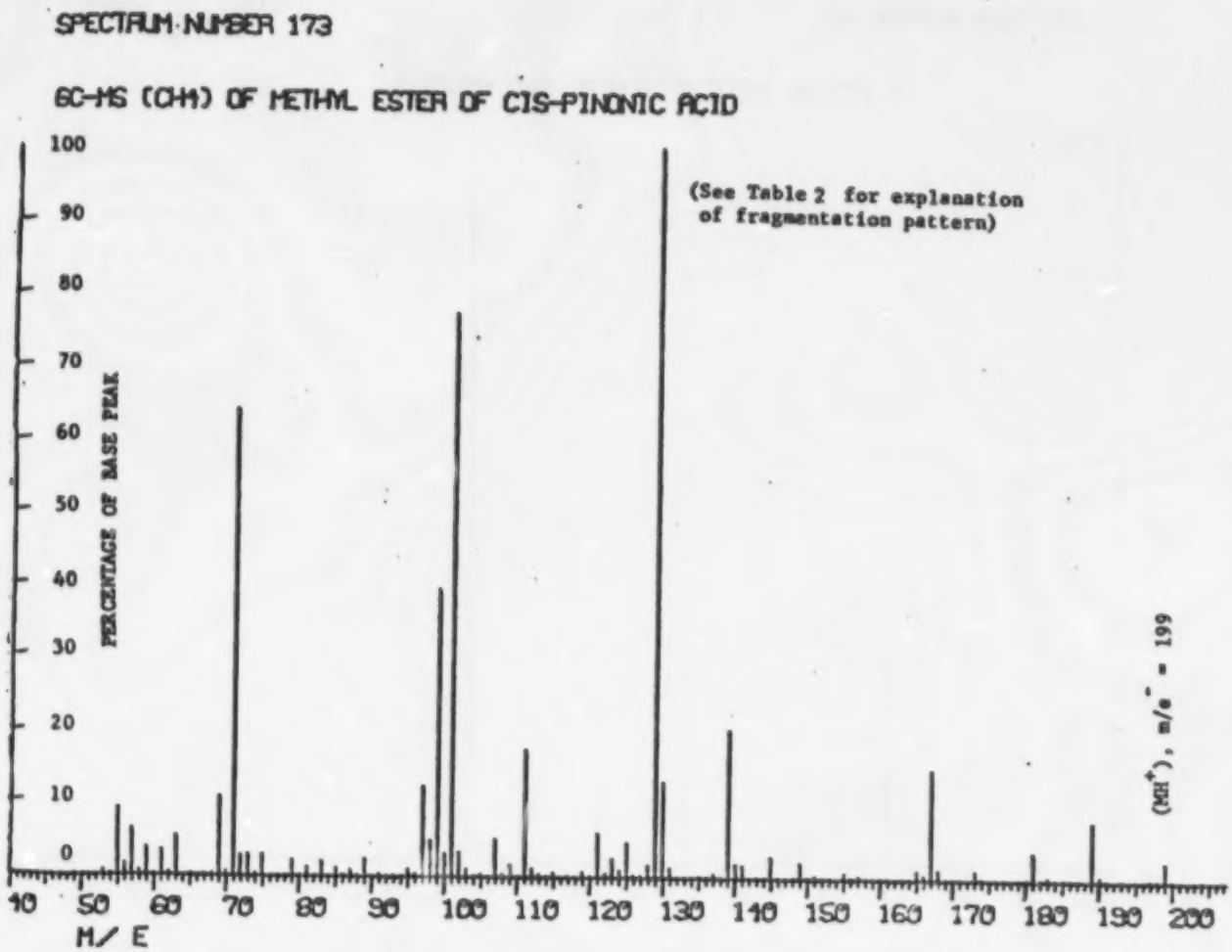
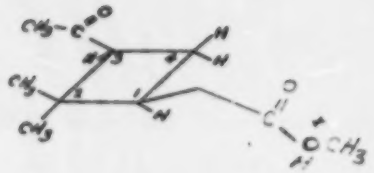


FIGURE 24. CHEMICAL IONIZATION MASS SPECTRUM OF AUTHENTIC METHYL CIS-PINONATE



Protonated parent-ion of methyl pinonate, $(MH)^+$, m/e$^-$ = 199

Fragmentation of Parent-Ion

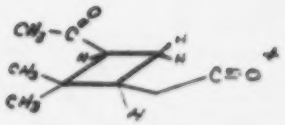
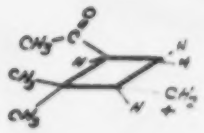
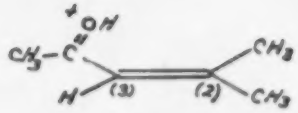
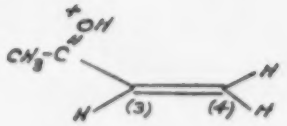
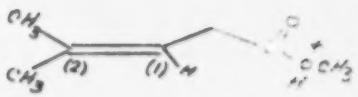
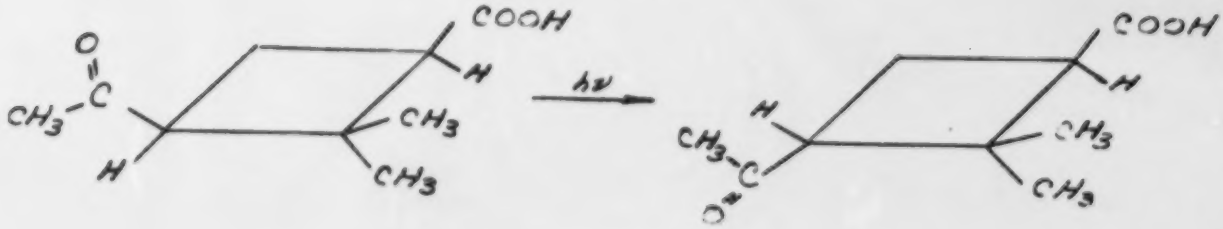
Process	Fragment	m/e$^-$
Loss of $H_2O(MH^+-18)$	-------	181
Loss of $CH_3OH(MH^+-32)$		167
Loss of $HCOOCH_3(MH^+-60)$		139
Transannular cleavage		111
Transannular cleavage		99
Transannular cleavage		71
Transannular cleavage		129

TABLE 2. FRAGMENTATION OF METHYL PINONATE UNDER CONDITIONS OF CHEMICAL IONIZATION (METHANE) MASS SPECTROMETRY

trans-pinonic acid may be present along with the more abundant cis isomer. Interconversion of the isomers in the presence of ultraviolet irradiation can be postulated. Tentative identification of the chromatographic peaks corresponding to the isomeric pinonic acids is indicated on the reconstructed gas chromatogram in Figure 25.

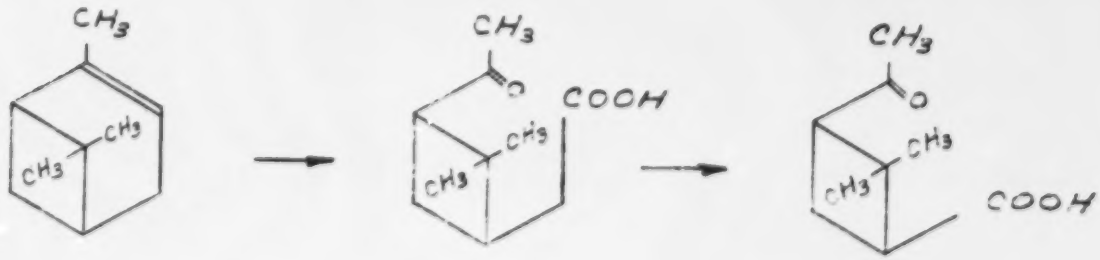


cis-pinonic acid

trans-pinonic acid

Tentative identification of the secondary reaction product of α-pinene has been made. The compound corresponds to Peak A of the reconstructed gas chromatogram in Figure 25. The mass spectrum of this compound is shown in Figure 26. The compound is tentatively identified as the homologous acid resulting from oxidative decarboxylation of pinionic acid, 2, 2-dimethyl-3-acetyl cyclobutanecarboxylic acid. The compound is hereinafter referred to as "nor-pinonic" aicd. Its mass spectral fragmentation pattern is rationalized in Table 3.

Thus we see that under the simulated atmospheric conditions of the smog chamber, α-pinene undergoes oxidative cleavage to pinonic acid. The pinonic acid produced may then be oxidatively decarboxylated (tentative) to the next lower homologous acid.



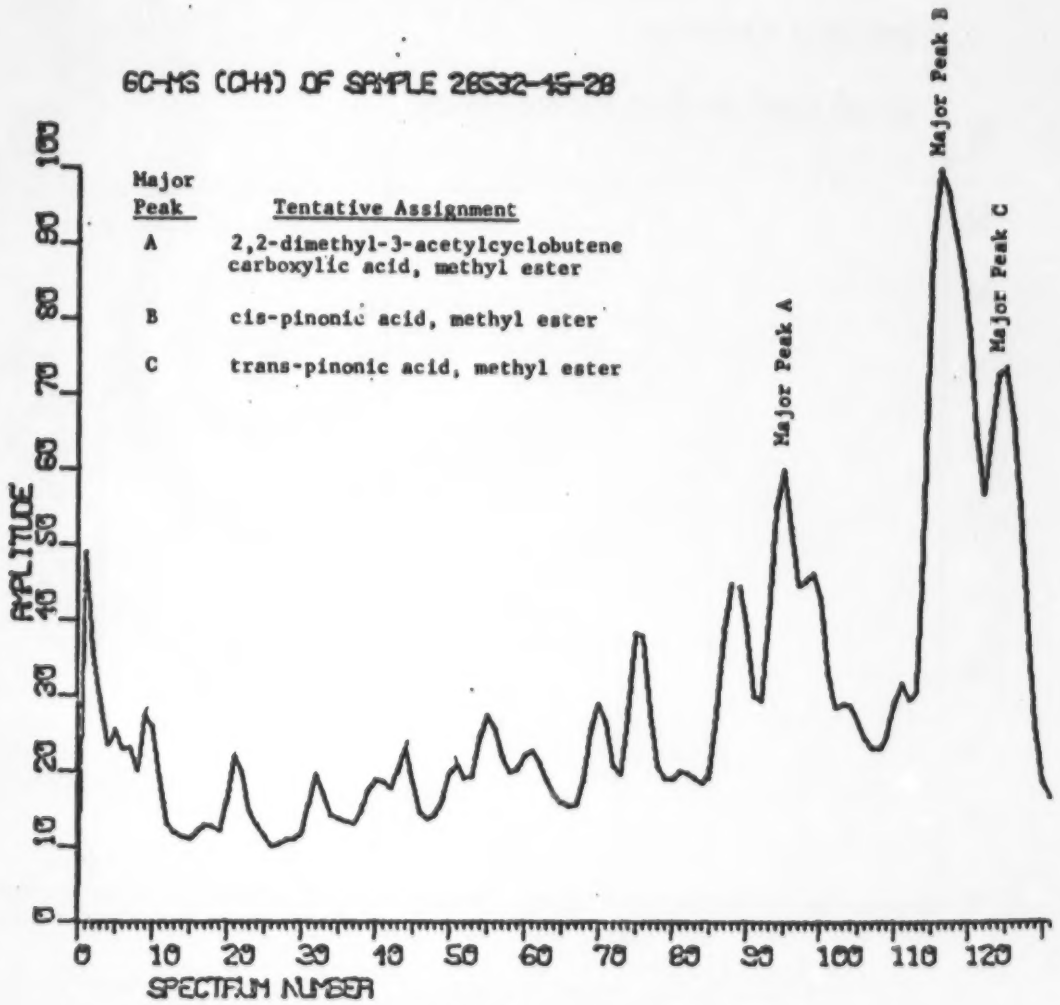
α-pinene

pinonic acid

"nor-pinonic" acid

```
SYSTEM 150 IS ON
SELECT MODE:  CONT
CALIBRATE?:
TITLE:  GC-MS (CH4) OF SAMPLE 28532-45-28
CALIBRATION FILE NAME:  CAL-H
FILE NAME:  27-2
MASS RANGE: 50-350
INTEGRATION TIME: 17
SAMPLES/AMU:  1
THRESHOLD:  1
1015 RANGE SETTING?:  H
MAX RUN TIME: 30
```

```
SYSTEM 150 IS ON
SELECT MODE:  OUTP
PRINT?:
PLOT?:
RECONSTRUCTED GAS CHROMATOGRAM?:  Y
FILE NAME:  27-2
LIMITED MASS RANGE?:  Y
MASS RANGE: 70-350
PRINT?:
EXPAND BY:
```



Major Peak	Tentative Assignment
A	2,2-dimethyl-3-acetylcyclobutene carboxylic acid, methyl ester
B	cis-pinonic acid, methyl ester
C	trans-pinonic acid, methyl ester

FIGURE 25. RECONSTRUCTED GAS CHROMATOGRAM OF α-PINENE REACTION PRODUCTS (Second Analysis)

```
SYSTEM 150 IS ON
SELECT MODE:  OUTP
PRINT?:
PLOT?:  Y
FILE NAME:  27-2
SPECTRUM NUMBER:  95
AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?: Y
BACKGROUND FILE NAME: 27-2
SPECTRUM NUMBER:  91
BACKGROUND AMPLIFICATION:
NORMALIZE ON:
```

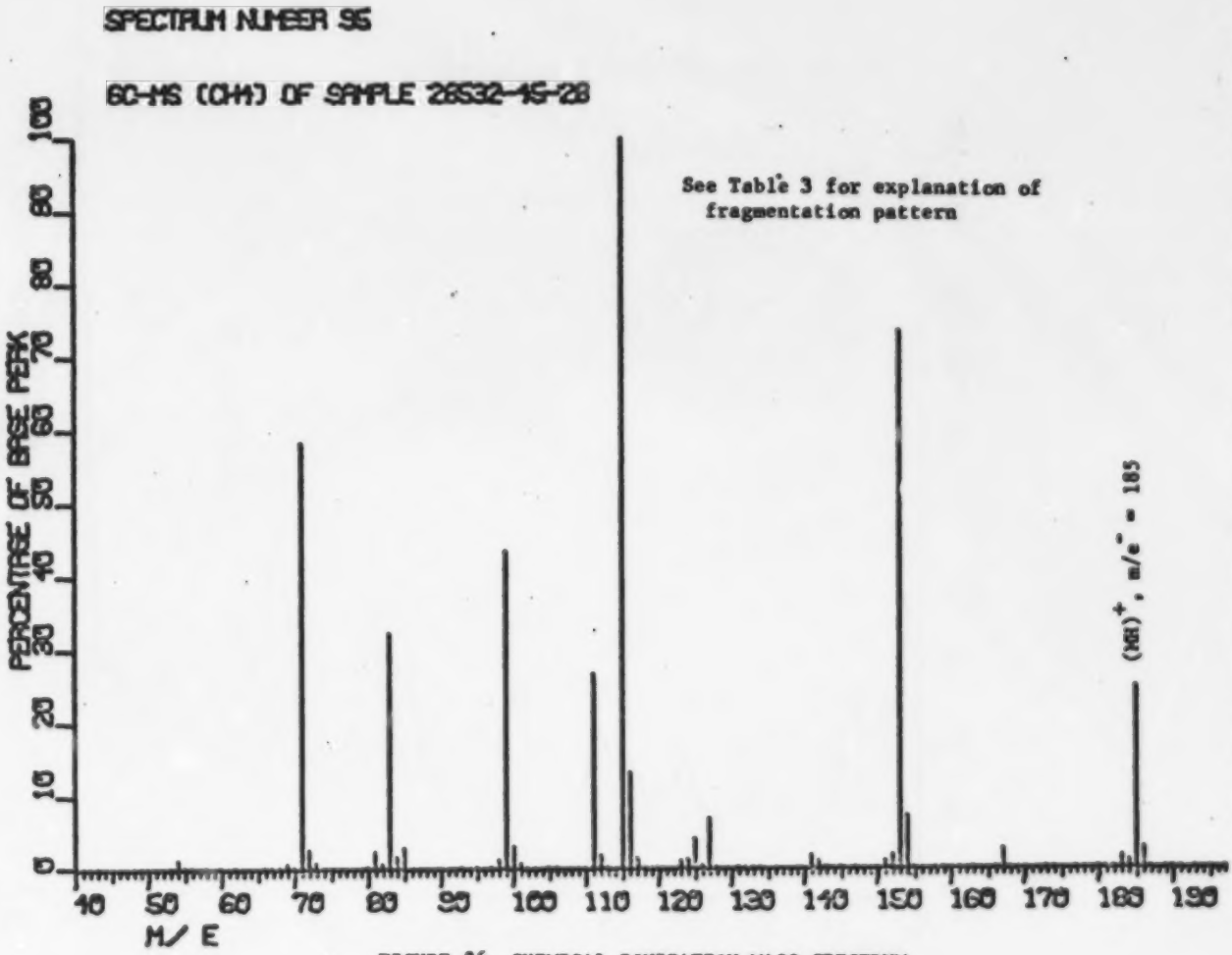
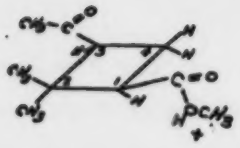


FIGURE 26. CHEMICAL IONIZATION MASS SPECTRUM OF GAS CHROMATOGRAPHIC PEAK (A)

(Refer to Figure 25)



Protonated parent-ion of methyl "nor-pinonate", $(MH)^+$, $m/e^- = 185$.

Fragmentation of Parent-Ion

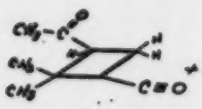
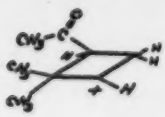
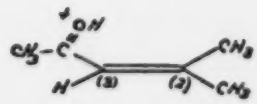
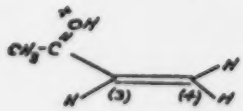
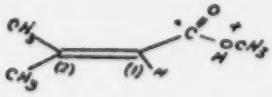
Process	Fragment	m/e⁻
Loss of $H_2O(MH^+-18)$	--	167
Loss of $CH_3OH(MH^+-32)$		153
Loss of $HCOOCH_3(MH^+-60)$		125
Transannular cleavage		111
Transannular cleavage		99
Transannular cleavage		71
Transannular cleavage		115

TABLE 3. FRAGMENTATION OF TENTATIVELY IDENTIFIED METHYL "NOR-PINONATE" UNDER CONDITIONS OF CHEMICAL IONIZATION (METHANE) MASS SPECTROMETRY

Aerosol in Natural Haze

In light of the above findings, the presence of pinonic acid was sought in air particulate collected at Smoky Mountains sampling site. The organic acid fraction of the particulate matter was isolated as described above. A portion of the isolated acid was treated with diazomethane and the methyl esters produced were analyzed by GC/MS. The reconstructed gas chromatogram is shown in Figure 27. The mass spectrum shown in Figure 28 identifies the indicated peak as corresponding to pinonic acid.

The presence of pinonic acid was similarly sought in urban air particulate collected at the Cooper Union sampling site. No detectible concentration of the compound could be found in air particulate from this source.

In summary, α-pinene, a natural terpene present in forest atmosphere, was reacted under simulated atmospheric conditions in the smog chamber. Two reaction products of α-pinene were isolated and identified as pinonic acid, and "nor-pinoic" acid (2,2-dimethyl-3-acetyl-cyclobutanecarboxylic acid.) Pinonic acid was found to be present in rural air particulate, but could not be found in urban air particulate.

Aerosol Generated from 1-Heptene

The aerosol generated from 1-heptene was collected, and the organic acid fraction was isolated, esterified with diazomethane, and analyzed by GC-MS. The reconstructed gas chromatogram is shown in Figure 29. Mass spectra of the compounds corresponding to chromatographic peaks (C) and (D) are shown in Figures 30 and 31. Both spectra exhibit protonated parent ions consistent with methyl hexenoate, $C_5H_9COOCH_3$ (isomeric, unsaturated acid-esters). Peaks consistent with loss of methanol and loss of methyl formate are also observed in both of these spectra. Tentative assignment of these compounds as isomers of methyl hexenoate is reasonable on the basis of the mass spectra.

Mass spectra for chromatographic peaks (A) and (B) exhibit protonated parent-ions peaks (see Figures 32 and 33) consistent with methyl pentenoate, $C_4H_7COOCH_3$ (isomeric, unsaturated acid-esters). Peaks for the parent-ion plus C_3H_5 are also observed. Although both spectra show peaks (very weak) consistent with loss of methyl formate, neither spectrum shows a peak for loss of methanol.

```
SYSTEM 150 IS ON
SELECT MODE:  IFSS
CALIBRATE?:
TITLE:  GC-MS (CH4) OF NATURAL HAZE  OV-17.
CALIBRATION FILE NAME:  CAL-H
FILE NAME:  23-2
MASS RANGE: 70-350
SAMPLES/AMU:  1
MAX RPT COUNT:  4
BASE INTEGRATION TIME:  8
RPT COUNT BEFORE CHECKING LOWER THRESHOLD:  4
LOWER THRESHOLD:  3
UPPER THRESHOLD:  4
1015 RANGE SETTING?:  H
MAX RUN TIME: 40
```

Reproduced from best available copy.

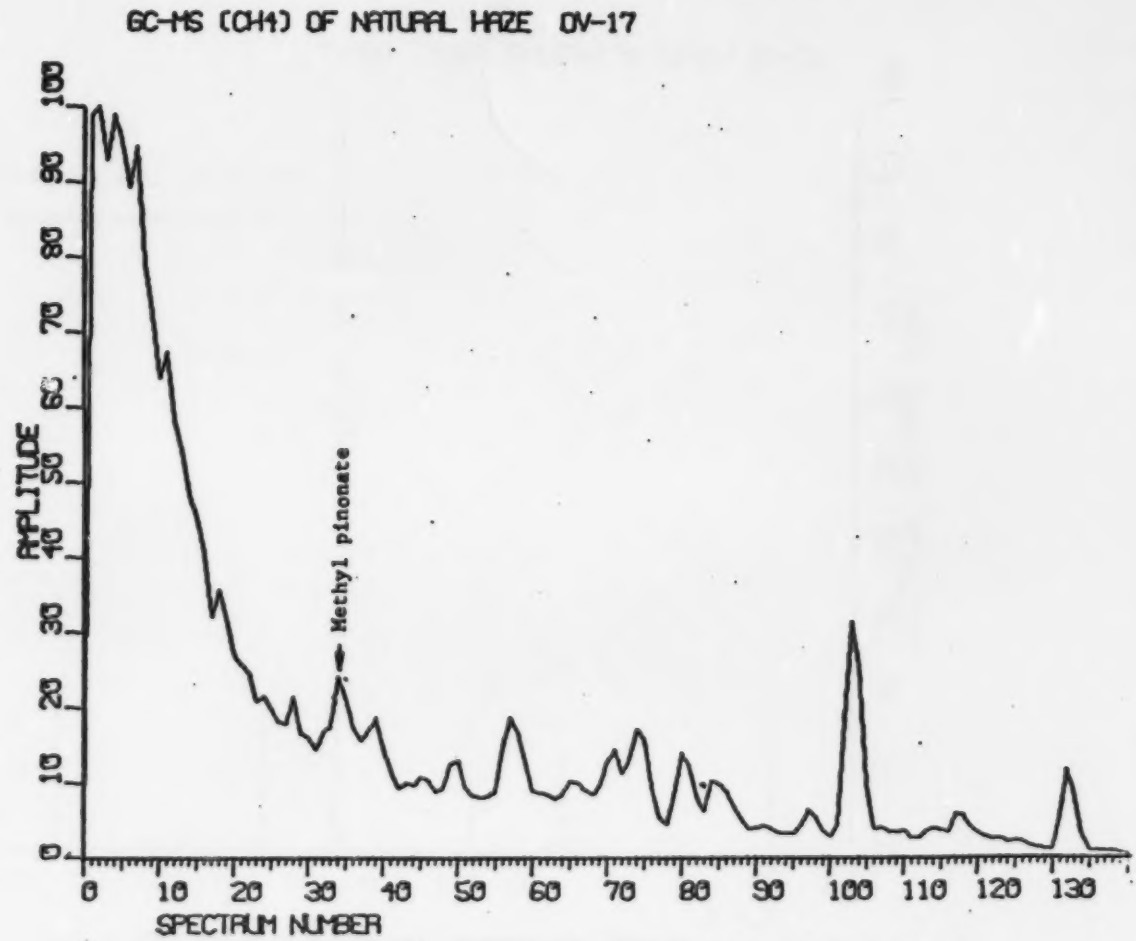


FIGURE 27. RECONSTRUCTED GAS CHROMATOGRAMS OF METHYL ESTERS OF ORGANIC ACIDS ISOLATED FROM NATURAL-HAZE AEROSOL

```
SYSTEM 150 IS ON
SELECT MODE:  OUTP
PRINT?:
PLOT?:  Y
FILE NAME:  23-2
SPECTRUM NUMBER:  34
AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?:  Y
BACKGROUND FILE NAME:  23-2
SPECTRUM NUMBER:  31
BACKGROUND AMPLIFICATION:
NORMALIZE ON:
```

Reproduced from best available copy.

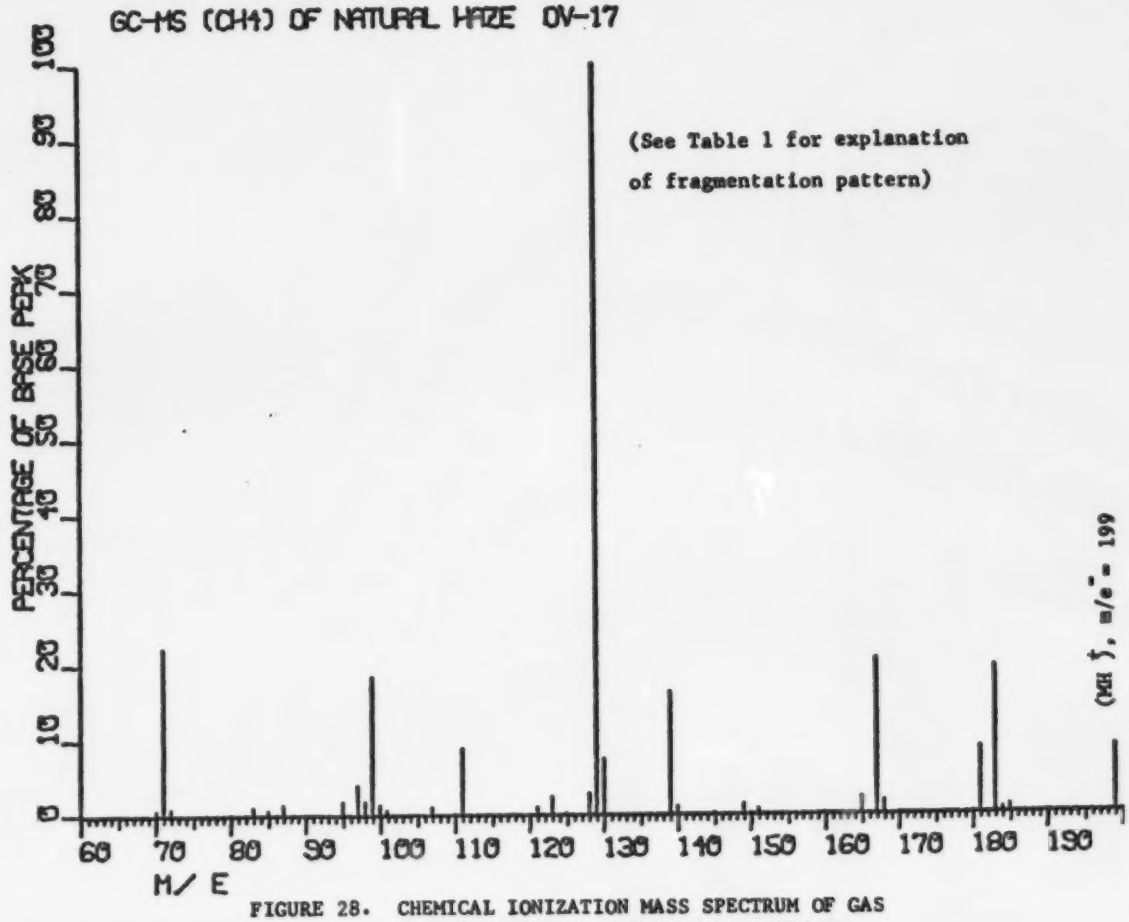


FIGURE 28. CHEMICAL IONIZATION MASS SPECTRUM OF GAS CHROMATOGRAPHIC PEAK CORRESPONDING TO PINONIC ACID

(Refer to Figure 27)

```
SYSTEM 150 IS ON
SELECT MODE:  IFSS
CALIBRATE?:
TITLE:  GC-MS (CH4) OF HEPTENE - NO2 PRODUCTS
CALIBRATION FILE NAME:  CAL-M
FILE NAME:  24-4
MASS RANGE:  50-250
SAMPLES/AMU:  1
MAX RPT COUNT:  4
BASE INTEGRATION TIME:  8

RPT COUNT BEFORE CHECKING LOWER THRESHOLD:  4
LOWER THRESHOLD:  3
UPPER THRESHOLD:  4
1015 RANGE SETTING?:  H
MAX RUN TIME:  30
```

Reproduced from best available copy.

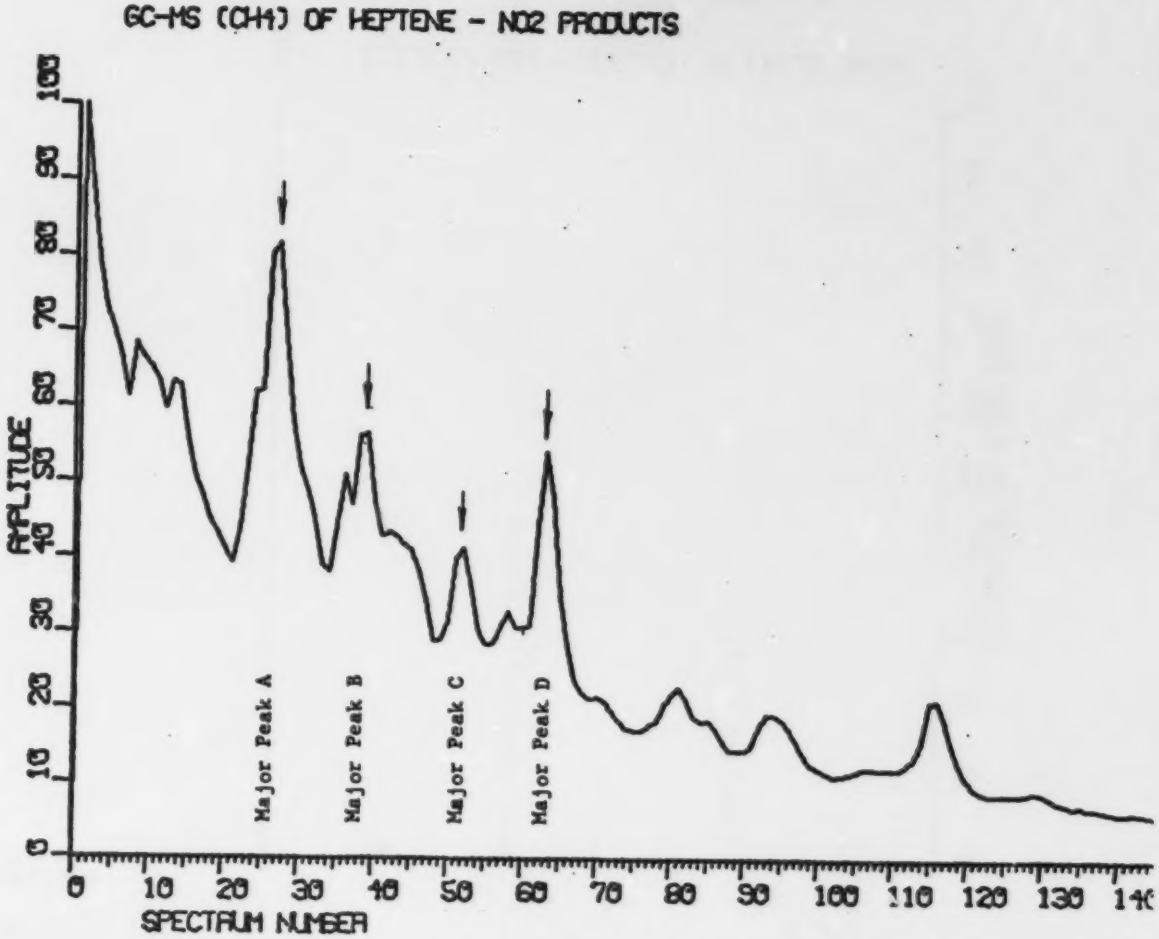


FIGURE 29. RECONSTRUCTED GAS CHROMATOGRAM OF 1-HEPTENE REACTION PRODUCTS

SYSTEM 150 IS ON
SELECT MODE: OUTP
PRINT?:
PLOT?: Y
FILE NAME: 24-4
SPECTRUM NUMBER: 52
AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?: Y
BACKGROUND FILE NAME: 24-4
SPECTRUM NUMBER: 48
BACKGROUND AMPLIFICATION:
NORMALIZE ON:

Tentative assignment:

$C_5H_9COOCH_3$

methyl hexenoate

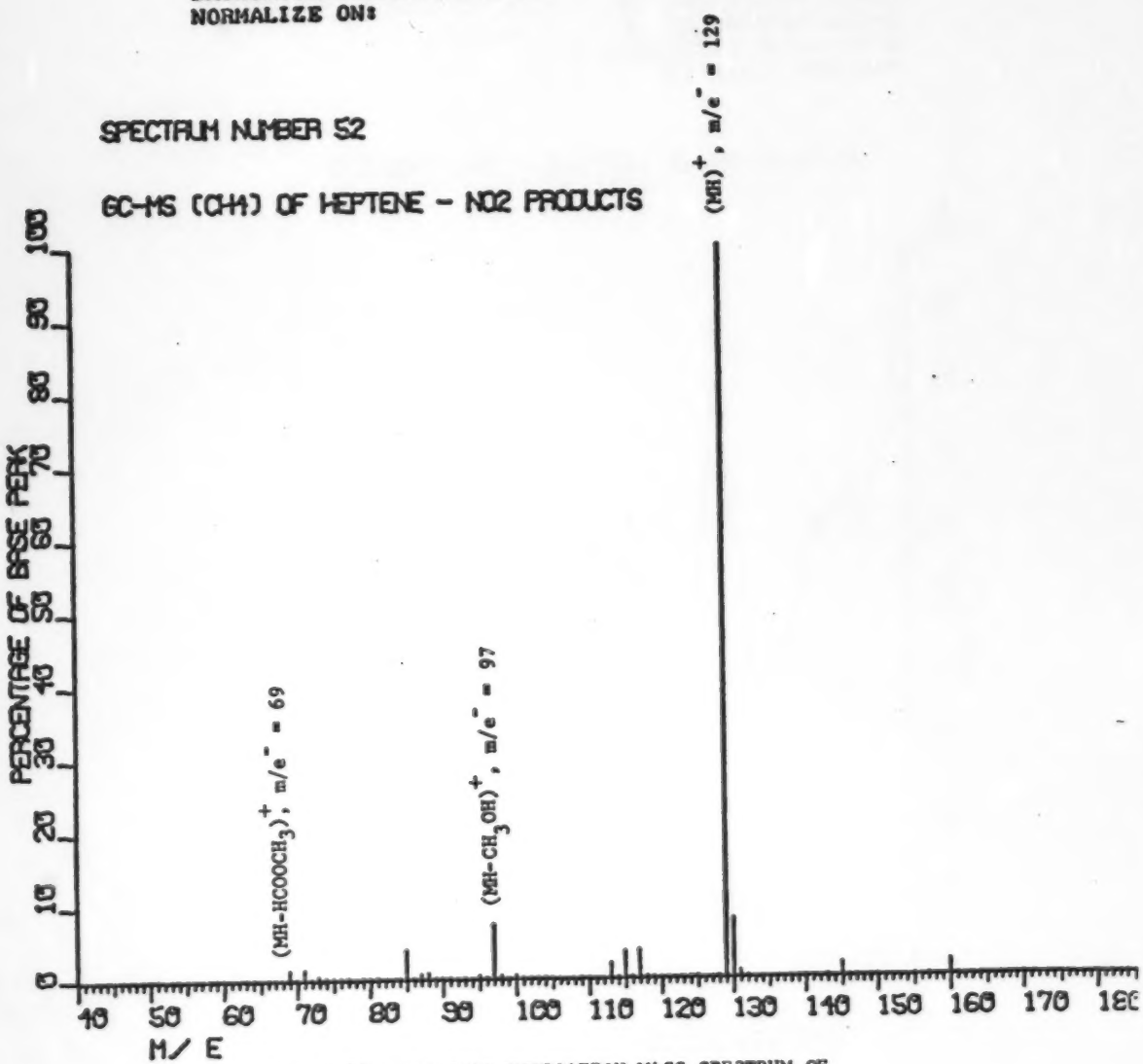


FIGURE 30. CHEMICAL IONIZATION MASS SPECTRUM OF GAS CHROMATOGRAPHIC PEAK (C)

(Refer to Figure 29)

SYSTEM 150 IS ON
SELECT MODE: OUTP
PRINT?:
PLOT?: Y
FILE NAME: 24-4
SPECTRUM NUMBER: 63
AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?: Y
BACKGROUND FILE NAME: 24-4
SPECTRUM NUMBER: 59
BACKGROUND AMPLIFICATION:
NORMALIZE ON:

59

Tentative assignment:

$C_5H_9COOCH_3$

methyl hexenoate

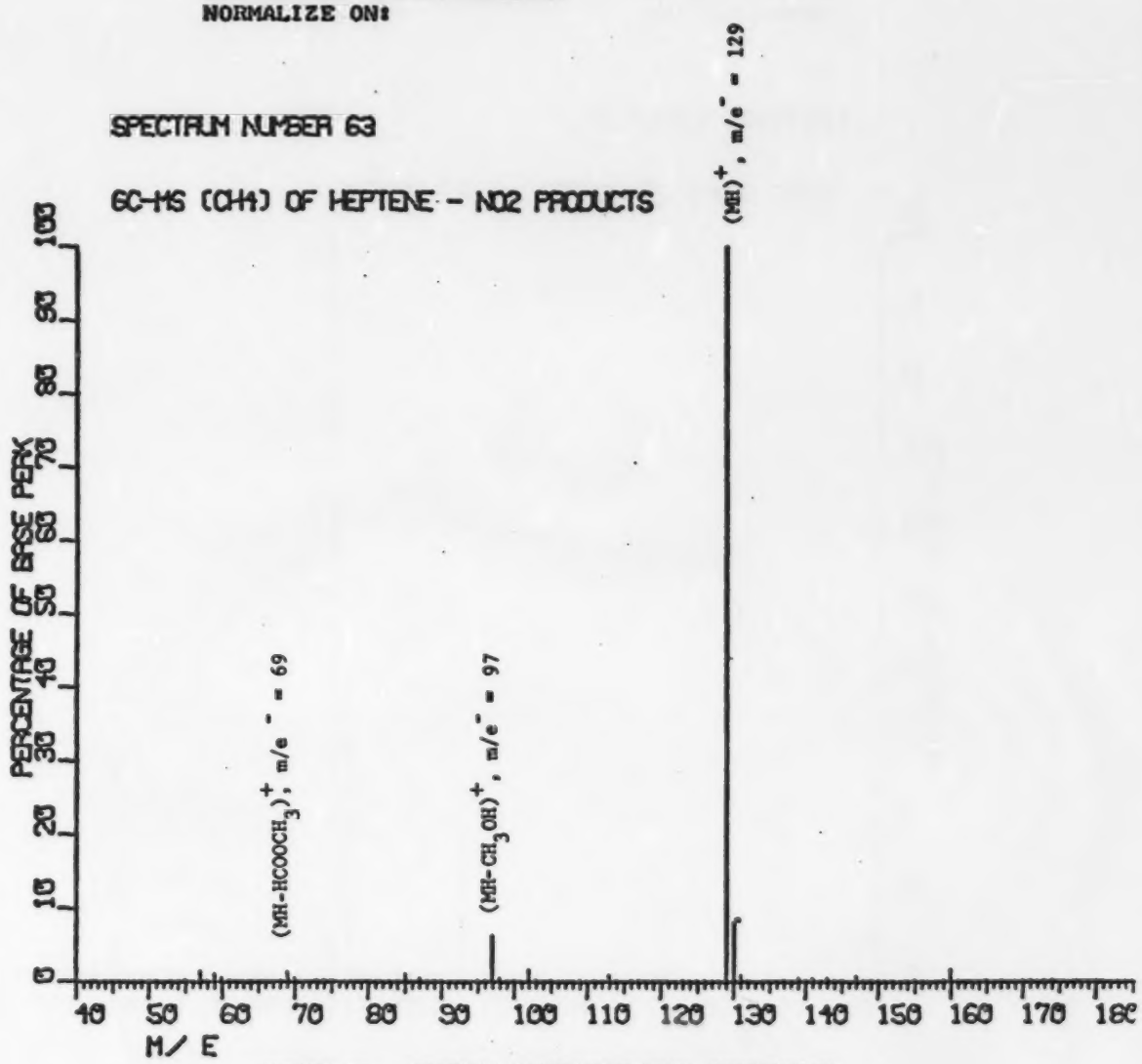


FIGURE 31. CHEMICAL IONIZATION MASS SPECTRUM OF GAS CHROMATOGRAPHIC PEAK (D)

(Refer to Figure 29)

```
                    OUTP
PRINT?:
PLOT?:  Y
FILE NAME:  24-A
SPECTRUM NUMBER:  27
AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?: Y
BACKGROUND FILE NAME: 24-A
SPECTRUM NUMBER:  21
BACKGROUND AMPLIFICATION:
NORMALIZE ON:
```

Tentative assignment:

$C_4H_7COOCH_3$

methyl pentenoate

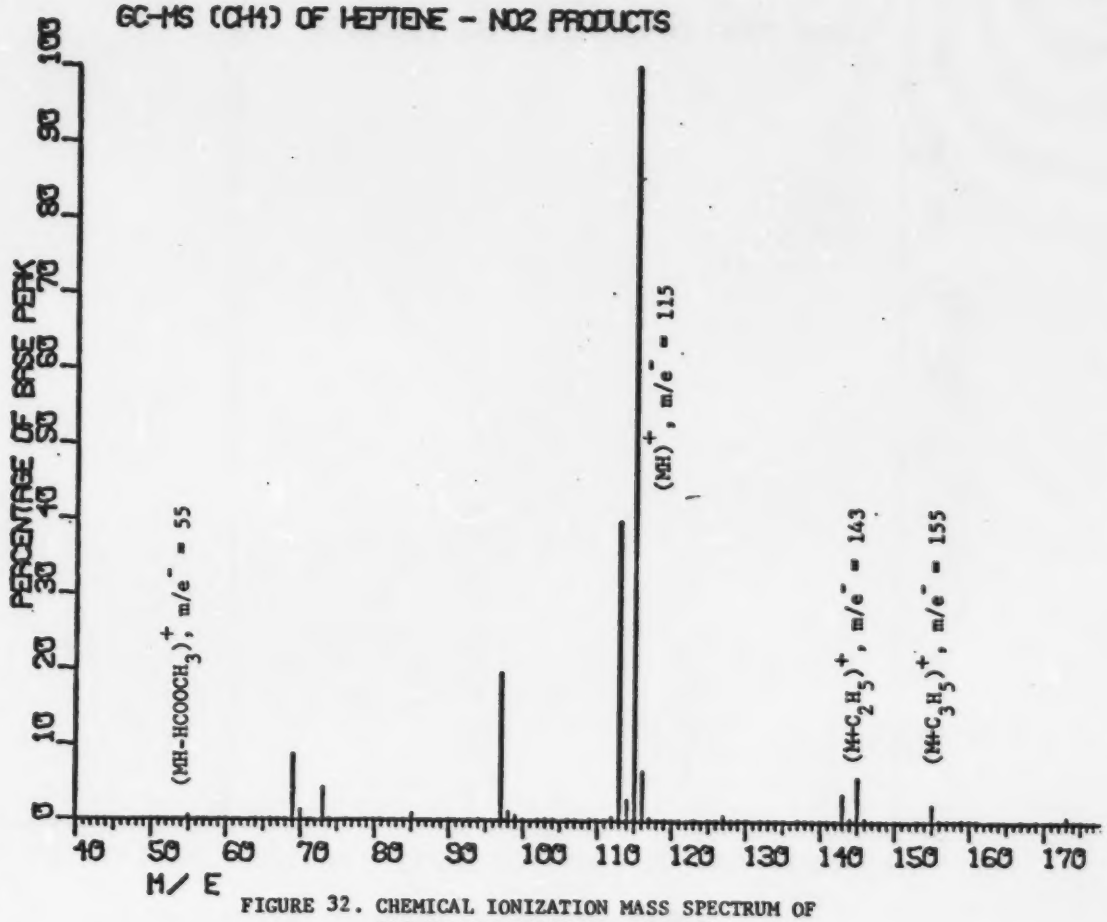


FIGURE 32. CHEMICAL IONIZATION MASS SPECTRUM OF GAS CHROMATOGRAPHIC PEAK (A)

(Refer to Figure 29)

```
SYSTEM 150 IS ON
SELECT MODE:  OUTP
PRINT?:
PLOT?:  Y
FILE NAME:  24-4
SPECTRUM NUMBER:  39
AMPLITUDE EXPANSION?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND?: Y
BACKGROUND FILE NAME: 24-4
SPECTRUM NUMBER:  34
BACKGROUND AMPLIFICATION:
NORMALIZE ON:
```

Tentative assignment:

$C_4H_7COOCH_3$

methyl pentenoate

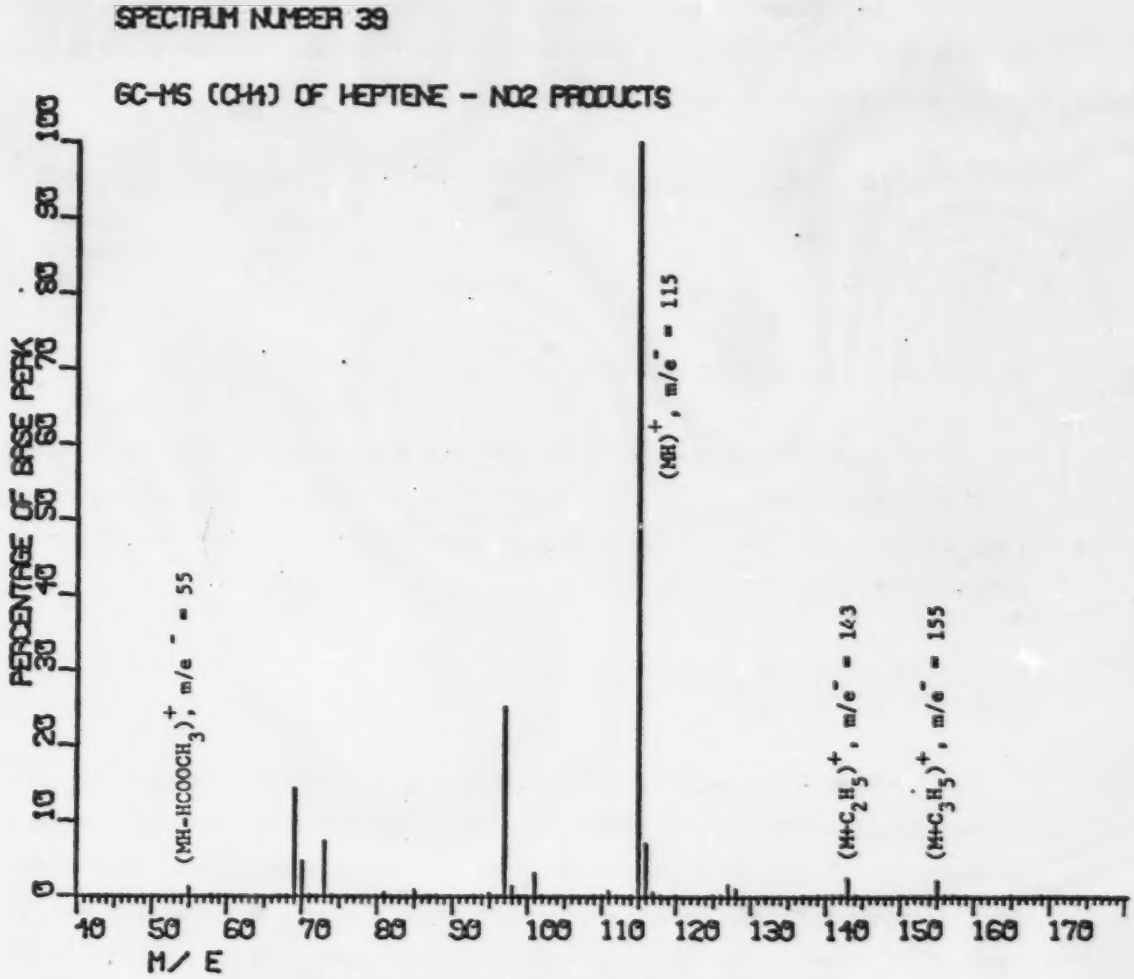


FIGURE 33. CHEMICAL IONIZATION MASS SPECTRUM OF GAS CHROMATOGRAPHIC PEAK (B)
(Refer to Figure 29)

Such a peak is to be expected in the spectra of methyl esters. Thus, the identification of these two compounds as isomers of methyl pentenoate is especially tentative.

Various positional isomers of hexenoic or pentenoic acid are possible. The α-β unsaturated isomer will display an ultraviolet absorption band at ~215 nm. The ultraviolet spectrum of the total acid fraction shows absorption in this region. Thus, the acid mixture probably includes α-β unsaturated acid.

In summary then, the data tends to indicate that irradiation of 1-heptene and NO_x in the smog chamber yields products including mixed hexenoic acids and (possibly) mixed pentenoic acids.

$$CH_3\text{-}(CH_2)_4\text{-}CH{=}CH_2 \xrightarrow{\text{(tentative)}} \underset{\substack{\text{mixed}\\\text{pentenoic}\\\text{acids}}}{C_4H_7COOH} + \underset{\substack{\text{mixed}\\\text{hexenoic}\\\text{acids}}}{C_5H_9COOH}$$

Aerosol Generated from Toluene

Analysis of auto exhaust particulate revealed the presence of benzoic acid and phenylacetic acid. In view of this finding, toluene was reacted in the smog chamber and the acid fraction of the aerosol produced was analyzed. Analysis failed to reveal a detectable concentration of benzoic acid.

Cross-Contamination in Generation of Smog Chamber Aerosol

Battelle's 610-cu. ft. environmental chamber was used to generate aerosol from a variety of pure compounds. In the operation of such a facility, aerosol is cleared from the chamber at the conclusion of the experiment by purging with purified air. In this program, purging was carried out for a minimum of 12 hours. Our results indicate that such purging may not be sufficient to remove all aerosol components from the chamber in preparation for subsequent experiments.

Aerosol was generated from the several pure compounds listed below in the following chronological order:

(1) α-pinene
(2) isoprene
(3) cyclohexene
(4) 1-heptene
(5) toluene .

As discussed previously in this report, GC-MS analysis of aerosol generated from α-pinene revealed the presence of pinonic acid. However, the analysis of aerosols subsequently generated from other precursors similarly revealed the presence of this acid. Specifically, pinonic acid was found in aerosol generated from isoprene, cyclohexene, and toluene. Presumably, this crystalline nonvolatile acid was not completely removed from the smog chamber by the purging procedure described above, and thus appears in aerosol subsequently generated from other precursors.

Based on the above data, it appears that the generally accepted purge procedure employed in this program may not effectively remove some components of generated aerosol. Alternate procedures should be examined in future work.

Summary: Organic Reactions in the Smog Chamber

In the analysis of the smog chamber reaction products, the involvement of two general types of reactions have been observed: oxidative cleavage of an olefinic bond and oxidative decarboxylation. The detailed reaction mechanisms involved cannot be postulated at this point. However, in cleavage of the olefinic bond, formation of a classical ozonide is probably involved rather than some unspecified free radical mechanism. The oxidative decarbonylation, on the other hand, may well involve a free radical mechanism.

Analysis for Polynuclear Aromatic Hydrocarbons

High-pressure liquid chromatography (HPLC) was evaluated for use in the separation and analysis of polynuclear aromatic hydrocarbons present in air and auto exhaust particulate. It was the objective of this phase of the study to develop a method whereby a rapid quantitative analysis of a series of PNA's might be conducted. From such data a ratio of PNA's present could be calculated. It has been suggested that such a PNA ratio might be useful in determining the automotive contribution to atmospheric pollution. However, this effort was discontinued at the direction of the Task Force in order that more general organic analyses might be carried out. The results obtained, however, demonstrate the capability of this technique to separate rapidly a variety of PNA's.

Work was conducted using a Waters Associates Model 100 ALC Automatic Liquid Chromatograph equipped with an ultraviolet photometric detector. The following materials were used to prepare chromatographic columns for evaluation.

(1) Oxypropionitrile (OPN) on Porosil C (Waters Associates)

(2) Zipax chromatographic support coated with a hydrocarbon polymer stationary phase (Du Pont)

(3) Corasil porous glass beads (Waters Associates)

(4) 20 percent Acetylated Cellulose (Machery, Nagel & Company)

(5) CPG 10-240 Corning Glass Beads treated with octadecyltrichlorosilane to yield a bonded hydrocarbon stationary phase.(7)

The chromatogram in Figure 34 shows the separation of several authentic PNA's. The separation was performed using a 1/8-in. stainless

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(7) Ledford, C.J., Morie, G. P., Glover, C. A., "Separation of Polynuclear Aromatic Hydrocarbons in Cigarette Smoke by High Resolution Liquid Chromatography", Paper presented at the 23rd Tobacco Chemists' Research Conference, Philadelphia, Penna. (1969).

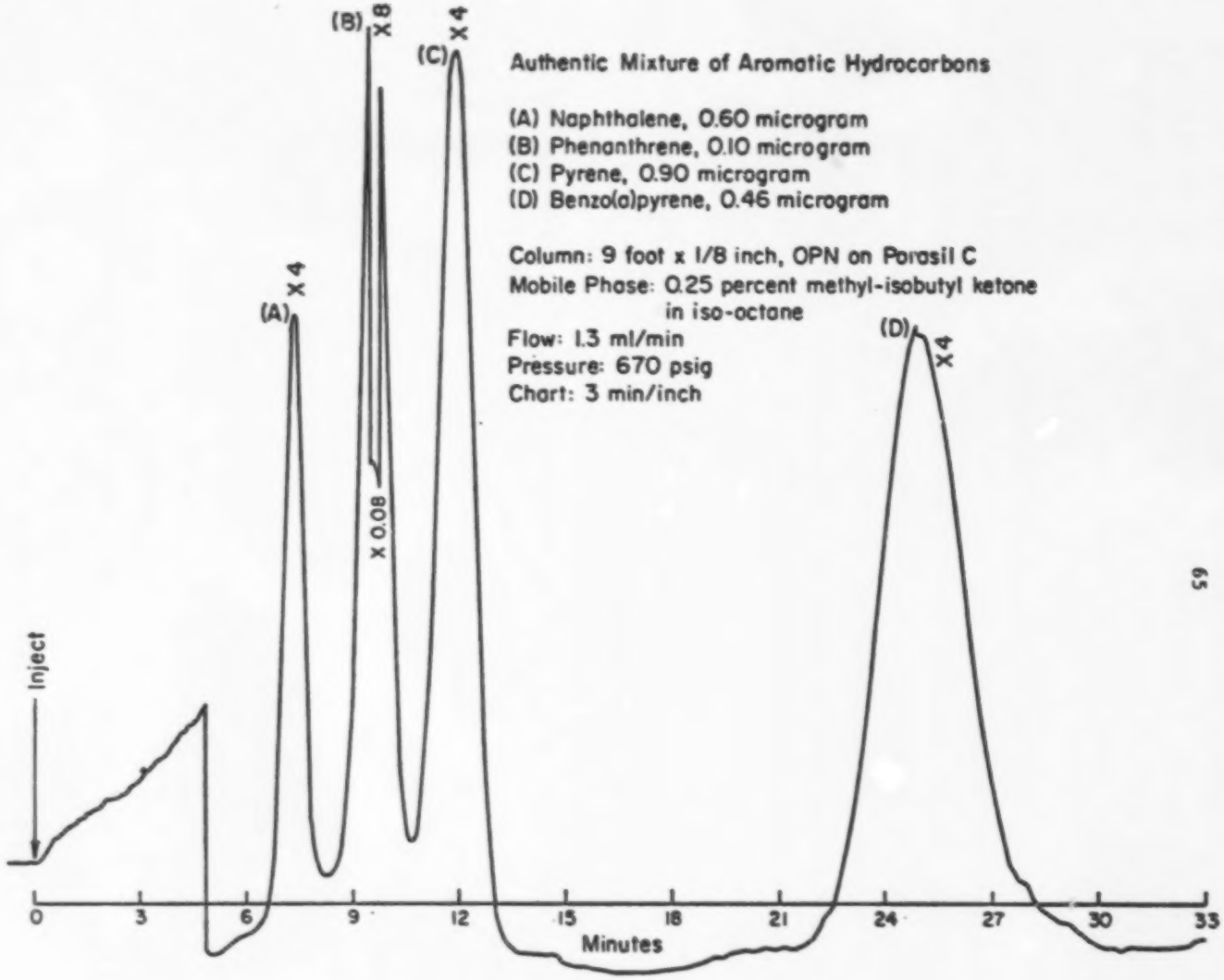

FIGURE 34. HIGH PRESSURE LIQUID CHROMATOGRAM OF AUTHENTIC POLYNUCLEAR AROMATIC HYDROCARBONS

steel column of OPN (oxypropionitrile)on Porasil C with a mobile phase of 0.25 percent methylisobutyl ketone in iso-octane. The column flow rate was 1.3 ml/min and the head pressure was 670 psig. Note that the time required for the separation shown is under 30 minutes and that the sensitivity obtained is well into the sub-microgram range.

The polynuclear aromatic hydrocarbon fraction of air particulate collected at the Cooper Union sampling site was analyzed using the above OPN column. The PNA fraction analyzed was isolated by preparative TLC on silica gel with chloroform as the developing solvent. The chromatogram in Figure 35 shows the separation of various components of the PNA fraction. Based on this analysis, a tentative identification of naphthalene, phenanthrene, and benzo-α-pyrene can be made. Note that the presence of pyrene is not indicated.

Further evaluation of the above OPN column was conducted. Specifically, a separation of benzo-α-pyrene and benzo-e-pyrene was attempted. Satisfactory resolution of the isomeric benzpyrenes was not realized. Thus, a column was sought which would yield such a separation. Chromatographic columns prepared from packing materials (2), (3), and (4) above did not resolve the benzpyrene isomers; these columns yielded separation of other PNA's, but were generally inferior to those already obtained using an OPN column.

A 9 ft x 1/8-inch column was prepared using CPG-10/240 Corning glass bead treated with octadecyltrichlorosilane (packing material No. 5 above). This column yielded good resolution of benzo-α-pyrene and benzo-e-pyrene from each other as well as from the lighter PNA's. The column was used with a mobile phase of acetonitrile at a flow rate of 0.57 ml/min and head pressure of 285 psig; the chromatogram is shown in Figure 36.

While giving good resolution of the isomeric benzypyrenes, this column is not as efficient as OPN on Porasil C for the resolution of the

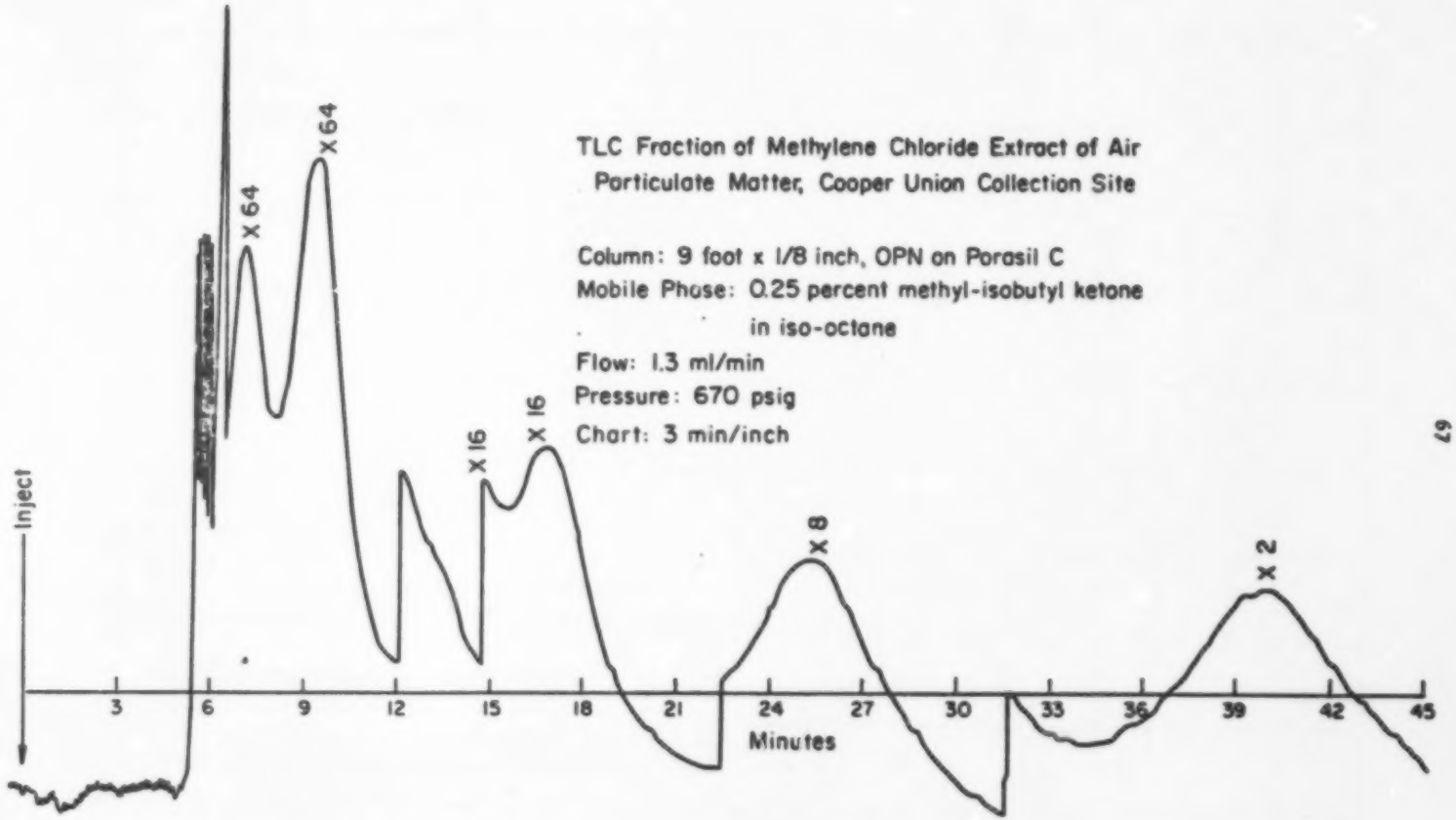

FIGURE 35. HIGH PRESSURE LIQUID CHROMATOGRAM OF TLC FRACTIONATED METHYLENE CHLORIDE EXTRACT OF AIR PARTICULATE MATTER

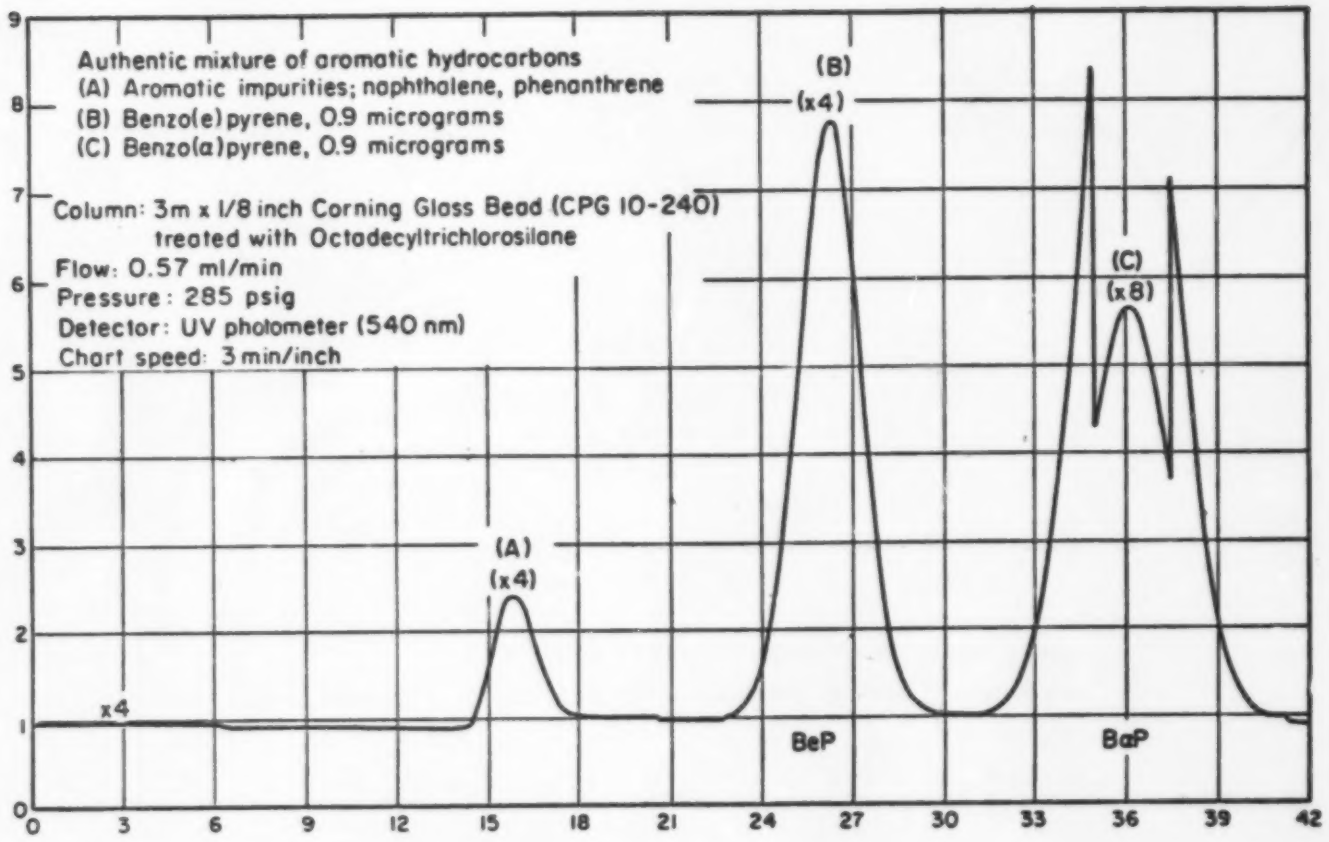
Authentic mixture of aromatic hydrocarbons
(A) Aromatic impurities; naphthalene, phenanthrene
(B) Benzo(e)pyrene, 0.9 micrograms
(C) Benzo(a)pyrene, 0.9 micrograms
Column: 3m x 1/8 inch Corning Glass Bead (CPG 10-240) treated with Octadecyltrichlorosilane
Flow: 0.57 ml/min
Pressure: 285 psig
Detector: UV photometer (540 nm)
Chart speed: 3 min/inch
(A) (x4)
(B) (x4)
(C) (x8)
x4
BeP
BαP
0 1 2 3 4 5 6 7 8 9
0 3 6 9 12 15 18 21 24 27 30 33 36 39 42

FIGURE 36. HIGH PRESSURE LIQUID CHROMATOGRAM OF AUTHENTIC POLYNUCLEAR AROMATIC HYDROCARBONS

lighter PNA's. Thus separate analyses using each column should be performed to obtain maximum analytical data.

INORGANIC ANALYTICAL STUDIES

Bronx Site

One sample, collected on a Millipore filter during a 23-hour period (9/30/70 to 10/1/70), was analyzed by spark-source mass spectroscopy for metals by atomic absorption for lead, and by wet-chemical methods for NO_3^-, $SO_4^=$, and NH_4^+. Results of analyses by spark-source mass spectrometry and atomic absorption are shown in Table 4; results of wet-chemical analyses are shown in Table 5. The percentage of lead is within the expected range. The proportion of sulfate relative to nitrate is higher than found in Los Angeles reflecting the higher SO_2 emissions in New York City. The ammonium concentration is also proportionately higher than found in Los Angeles. On a relative basis the amount was almost equivalent to the stoichiometric quantity required for the formation of NH_4NO_3 and $(NH_4)_2SO_4$.

Smoky Mountains Site

Quantitative analysis of aerosols collected in the Smoky Mountains has not yet been completed. However, sulfur and vanadium were found but lead was not present.

TABLE 4. METALS IN BRONX SAMPLES[(a)]

Metal	Percent of Total Sample Weight	Metal	Percent of Total Sample Weight
Al	5	Sn	0.15
Ca	5	Ni	0.15
Si	5	Mo	0.005
Fe	2.5	V	0.5
Mn	1	Cu	0.4
Ba	1	Ag	0.05
B	0.015	Zn	1
Mg	1.5	Na	1.5
Pb	1.5	Ti	0.35
Cr	0.05	Zr	0.005
Pb (by aa)	1.8		

(a) All analyses by spark-source mass spectroscopy accuracy ± 50 percent, with exception of Pb which was also analyzed by atomic absorption (aa).

TABLE 5. WET-CHEMICAL ANALYSIS OF BRONX SAMPLE

Component	Percent of Total Sample Weight	Relative Number of Radicals
NH_4^+	7.6	1
NO_3^-	13	0.5
$SO_4^=$	13	0.3

ACKNOWLEDGMENT

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